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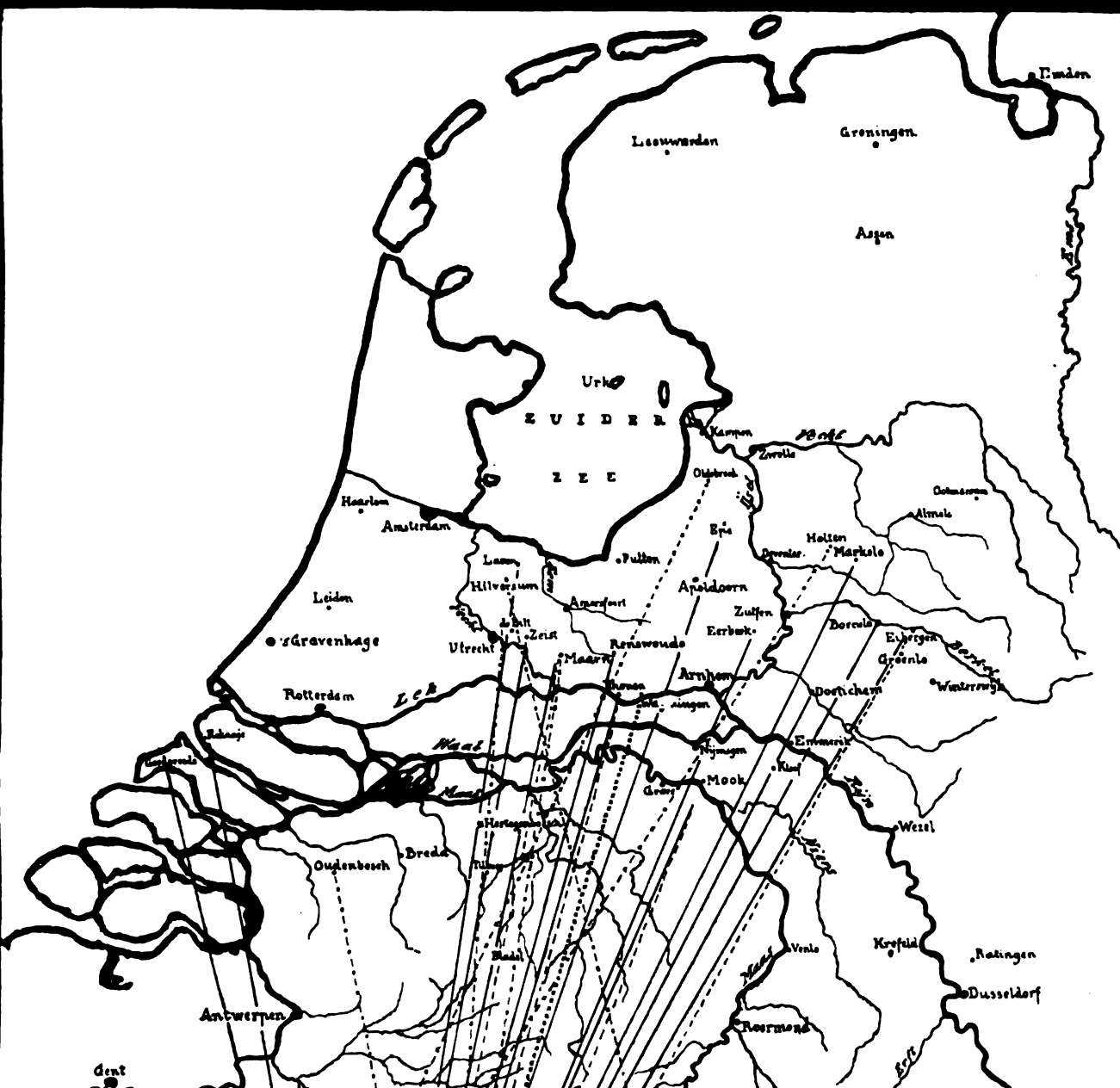
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TE AMSTERDAM.

PROCEEDINGS OF THE MEETING
of Saturday December 30, 1905.

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Chemistry. — "*The bromination of toluene*". By Prof. A. F. HOLLEMAN and Dr. F. H. VAN DER LAAN.

(Communicated in the meeting of October 28, 1905).

In the reaction between toluene and bromine we have a striking example of the influence exerted on the nature of the product of reaction by experimental conditions. About this the following is known:

1. *Influence of temperature.* In the dark and at a low temperature there is formed a mixture of bromotoluenes; on the other hand benzyl bromide is formed at the boiling point of toluene.

2. *Influence of light.* At a low temperature benzyl bromide is exclusively formed; the same takes place at the boiling temperature.

3. *Influence of catalyzers.* Through their action the bromination takes place exclusively in the core, even in full daylight and at an elevated temperature.

If we make a closer study of the papers which have appeared as to this reaction it strikes us, as in so many other cases, that the virtually known suffers from much uncertainty owing to an insufficient observance of the quantitative proportions. When, for instance, SCHRAMM states that on bromination in sunlight benzyl bromide is exclusively formed, a doubt arises as to the correctness of this view, as the only proof he adduces is that the boiling point of his product lies at 195°—205°; his boiling point limits are therefore so wide apart that they suggest rather the presence than the total absence of isomers. As regards the bromotoluenes formed in the reaction, it was known that these are *ortho*- and *para*-bromotoluene. But the question, in what proportion those are formed under the influence of the three above factors, has only been made the subject of greatly varying conjectures and rough estimates. Nothing was known also as to the nature of the products of reaction which are formed in the dark at temperatures between the ordinary and the boiling point of toluene (110°).

There was, therefore, every reason to again study this interesting reaction and to try to solve the following questions:

In how far is the composition of the reaction-mixture dependent 1. on the temperature; 2. on the action of light; 3. on the presence of catalyzers.

In my laboratory, first at Groningen, afterwards at Amsterdam, Dr. VAN DER LAAN has made a contribution to the resolution of these questions by means of a careful experimental research; he commenced

by making sure of the absolute purity of his toluene and bromine by means of special methods of purifying; for details his dissertation and his paper in the "Recueil" (next appearing) should be consulted.

As the composition of the reaction mixture consisting of *ortho*-*parabromotoluene* and benzyl bromide had to be determined, but as no method for this was available, it was necessary to work out a suitable process; in order to do this it was necessary to first possess the three said substances in a chemically pure state so as to be able to make artificial mixtures for testing the analytical methods.

The preparation of *parabromotoluene* and of benzyl chloride presented no difficulties. The first substance was obtained from *paratoluidine* by diazotation, and as this is a solid it could be readily freed from any adhering traces of its isomers by recrystallisation from ligroin and thus yield a *parabromotoluene* also free from its isomers. Benzyl bromide was made from benzyl alcohol and hydrobromic acid. On the other hand the preparation of pure *orthobromotoluene* was not so easy. This was also prepared from the corresponding toluidine, but the difficulty was to obtain the latter in a pure condition. This was overcome in the manner previously communicated (These Proc. VII p. 395).

In the actual investigation a large excess of toluene was always taken (8 mols. toluene to 1 mol. of bromine) so as to avoid for certain the formation of higher substitution products. Besides the three above mentioned substances the reaction mixture contains, therefore, a large quantity of toluene: hydrogen bromide is also present and often also a small quantity of free bromine, especially in the reactions which were executed in the dark. This reaction product was now analysed quantitatively as follows: A slow current of air removed almost quantitatively the hydrogen bromide, which was absorbed in water and titrated: the quantity thus found is equivalent to and serves as a measure for the brominated products. In order to free the liquid from any free bromine, and to determine the amount of the same, it is poured into a solution of potassium iodide and the liberated iodine titrated with thiosulphate. The liquid is now washed with water, dried, and the toluene is distilled off in an airbath heated by boiling amyl alcohol. On taking the sp. gr. of the distilled toluene it appeared that this had not carried over any brominated products to speak of.

After these operations the liquid now only consisted of the bromotoluenes and benzyl bromide besides also a small quantity of toluene. In this mixture the benzyl bromide can be estimated by means of alcoholic silver nitrate which yields silver bromide quantitatively.

In order to determine in what proportion *ortho*- and *para*bromotoluene are present, it was necessary to remove the benzyl bromide from the mixture. This was done by bringing it into contact with dimethylaniline. There is then formed quantitatively an ammonium bromide, the bulk of which is deposited as a crystalline mass. By washing the residual liquid with very dilute nitric acid the excess of dimethyl aniline and the still dissolved ammonium bromide are removed so that we obtain finally a liquid consisting merely of the bromotoluenes. When dried and distilled in vacuo it is ready for the determination of the isomers. This was done by determining the solidifying point of this purified liquid. By means of the solidifying point curve previously constructed by Dr. VAN DER LAAN, the composition of the mixture could be at once ascertained from the said point. By the analysis of a series of made up mixtures he was satisfied that this method of analysis gives results accurate within about 1 percent and is therefore sufficiently accurate for the purpose intended.

With the aid of the method described Dr. VAN DER LAAN obtained the following results.

1. *Influence of temperature.* The flask containing the mixture of bromine and toluene was kept carefully in the dark. Observations were made at 25°, 50°, 75° and 100°. At 25° the reaction took place very slowly and even after a week the bromine had not altogether disappeared. At 50° this was already the case in 3 days. The subjoined table contains the analyses of the reaction mixtures. The figures given are each the mean of 3 or 4 concordant determinations.

From this it appears that in the dark a regular increase of the benzyl bromide content takes place with a rising temperature. From a graphical extrapolation it appears that benzyl bromide is no longer formed below 17°, but, on the other hand, above 83° it is the sole reaction product. These conclusions, however, must still be confirmed experimentally. The proportion in which *ortho*- and *para*bromotoluene are formed also alters somewhat in favour of the first-named isomer. A determination of the sp. gr. of the mixture showed that this does not contain any of the higher brominated substances. The mixture obtained at 25° had a sp. gr. of 1.3598 at 64°.6 whilst a mixture of the two isomers in the same proportion shows a sp. gr. of 1.3598 at 64°.

2. *Influence of light.* As already observed, SCHRAMM claims to have obtained exclusively benzylbromide when brominating at low temperature in full sunlight, although his experimental data create

T A B L E I.

Temp.	Composition of the brominating product			Composition of the mixture	
	ortho bromotoluene	para	benzyl bromide	ortho + para bromotoluene	
25	35.5	53.9	10.6	39.7	60.3
50	23.5	32.8	43.7	41.8	58.2
75	6.2	7.5	86.3	45.3	54.7
100	—	—	100	—	—

some doubt about this. In diffuse daylight *ortho*- and *para*bromotoluene are also formed according to him; ERDMANN, on the other hand, stated that benzylbromide is the sole product. The observations of Dr. VAN DER LAAN confirm those of ERDMANN. In diffuse daylight the bromination proceeds very rapidly at 25°; in about 10 minutes all the bromine has disappeared. The analysis of the product gave 99% of benzylbromide. From this it follows that pure benzylbromide can be readily prepared in this manner. BEILSTEIN, who attempted this previously, arrived at the opposite result. This, however, was caused by the fact that he exposed to the light a mixture of bromine and toluene in equivalent proportions at the temperature of boiling toluene. Operating in this manner we obtain indeed a product without a constant boiling point which on fractionation appears to contain products boiling at higher temperatures. If, however, working in the light and at 100°, only one mol. of bromine is used for 10 mols. of toluene, the formation of these higher boiling substances is prevented. The excess of toluene is readily removed by distillation. After a distillation in vacuo Dr. VAN DER LAAN obtained a product solidifying at - 4°.3 of a sp. gr. 1.3887 at 65°.5 whilst these constants, according to his observations, are - 3°.9 and 1.3858 at 65°.5 for pure benzylbromide from benzylalcohol. The benzylbromide thus prepared contains, therefore, less than 0.5% of impurities.

3. *Influence of Catalyzers.* As the influence of light is, as we have seen, very great, all the experiments with catalyzers were made in complete darkness. Of these were tested: antimonytribromide, aluminiumbromide, ferricbromide and phosphorustribromide. Of the first three it is stated that they favour the bromination in the core, of the latter that it accelerates the formation of benzylbromide. The observations of Dr. VAN DER LAAN are in harmony with this. The

temperature at which the reaction was tried was 50°, and the action of the catalyzers was determined in such a manner that increasing quantities of them were added and the composition of the reaction product determined each time.

A feeble catalyzer was found in antimony tribromide as shown in the subjoined table.

T A B L E II.

Temp. 50°; 50 c.M.³ toluene + 3 c.M.³ bromine. Dark.

Mol SbBr ₃ on 1 mol Br ₂	Composition of the mixture ortho-para		Composition of the brominating product		
	ortho bromotoluene	para bromotoluene	ortho bromotoluene	para bromotoluene	benzyl bromide
0.00	41.8	58.2	23.5	32.8	43.7
0.0017	40.1	59.9	22.4	33.4	44.2
0.0084	38.9	61.1	24.0	37.8	38.2
0.016	38.3	61.7	26.0	42.0	32.0
0.034	38.9	61.1	28.0	44.1	27.9
0.089	—	—	—	—	18.7

The quantity of benzylbromide diminishes with increasing quantities of the catalyzer but is not inversely proportional; the decrease is much less. The proportion of *ortho*- and *para*bromotoluene undergoes but a slight modification.

Aluminiumbromide, however, acts very energetically, as very small quantities prevent the formation of benzylbromide. The experiments were conducted by adding a little aluminium powder to the mixture of toluene and bromine, thereby converting it rapidly into the bromide. The following figures were obtained :

T A B L E III.

Temp. 50°; 50 c.M.³ toluene + 2.5 c.M.³ bromine. Dark.

Mol AlBr ₃ on 1 mol Br ₂	Benzyl- bromide	Composition of the mixture.	
		ortho bromotoluene	para bromotoluene
0	43.7	41.8	58.2
0.002	43.1	43.9	56.1
0.004	0.5 (?)	44.6	55.4
0.006	0	44.3	55.7
0.017	0	49.2	50.1

Whereas SbBr_3 modifies the proportion of *ortho-para* slightly in favour of the *para* there is present here a much stronger influence of AlBr_3 in favour of the *ortho*.

Particularly interesting here is the influence on the amount of benzyl bromide. Although with only 0.002 mol. no modification of those proportions is perceptible, this becomes so pronounced with double the quantity that practically no more benzyl bromide is formed. This result is very striking and deserves a closer study.

With ferric bromide this phenomenon was repeated; this appeared to be a still more powerful catalyzer than aluminium bromide, as the limit of its activity is situated still considerably lower as may be seen from the subjoined table:

T A B L E IV.

Temp. 50° ; 50 cM.³ toluene + 2.5 cM.³ bromine. Dark.

Mol Fe Br_3 on 1 mol Br_2	Benzyl- bromide	Composition of the mixture.	
		<i>ortho</i>	<i>para</i> bromotoluene
0	43.7	41.8	58.2
0.0007	40.8	36.9	63.1
0.001	7.8	—	—
0.002	0	36.0	64.0
0.006	0	37.9	62.1
0.01	0	37.0	63.0

Here, the quantity of *ortho* is again depressed by the catalyzer.

With *phosphorus trichloride* as catalyzer Dr. VAN DER LAAN has only made one experiment which, in accordance with ERDMANN's investigation, gave an increase in the amount of benzyl bromide.

T A B L E V.

Temp. 51° ; 50 cM.³ toluene + 3 cM.³ bromine. Dark.

Mol P Br_3 on 1 mol Br_2	Benzyl- bromide	Bromotoluenes	
		<i>ortho</i>	<i>para</i>
0	45.4	41.8	58.2
0.02	54.7	41.4	58.6

The quantity of benzyl bromide has therefore, much increased but the proportion *ortho-para* has kept fairly well unaltered.

For further particulars as to these researches VAN DER LAAN'S original dissertation should be consulted. An article by him on this subject will also appear, shortly, in the "Recueil".

Amsterdam, Sept. '05. Chemical Laboratory of the University.

Geology. — "*On fragments of rocks from the Ardennes found in the Diluvium of the Netherlands North of the Rhine.*" By Prof. A. WICHMANN.

(Communicated in the meeting of November 25, 1905).

Ever since the 18th Century, the attention of geologists has been drawn to the boulders scattered about our heathgrounds and in opposition to the various and oftentimes curious theories started to account for their presence there, A. VOSMAER then already expressed the opinion that they had been transported from elsewhere by "A Mighty Flood".¹⁾ A little later, A. BRUGMANS²⁾ and after him S. J. BRUGMANS³⁾ pointed to Scandinavia as the original home of these erratics; but this view, though shared by a few other scientists, was not generally adopted until after the publication of J. F. L. HAUSMANN'S treatise⁴⁾. It seemed then as if the only question still remaining to be solved, was in what way and by what road this transport had been affected. Little or no thought was given to the possibility that other countries might be also accountable for their origin.

It was not until 1844 that W. C. H. STARING, whilst investigating the nature of these boulders, discovered that at least those composed of sandstone and quartzite, were found as well in the Ardennes, in the districts of Berg and Mark, at the foot of the Harz Mountains

1) JOHANNES VAN LIER. Oudheidkundige brieven, bevattende eene verhandeling, over de manier van Begraven, en over de Lijkbussen, Wapenen, Veld- en Eere-teekens der oude Germanen. Uitgegeven . . . door A. VOSMAER. 's-Gravenhage 1760, p. XV, 10, 11, 103.

2) Sermo publicus, de monumentis variarum mutatum, quas Belgii foederati solum aliquando passum fuit. Verhandelingen ter nasporing van de Wetten en Gesteldheid onzes Vaderlands. I. Groningen 1773, p. 504, 508.

3) Lithologia Groningana. Groningae 1781. Preface p. 2, 3.

4) Verhandelingen over den oorsprong der Graniet en andere primitieve Rotsblokken, die over de vlakten der Nederlanden en van het Noordelijk Duitschland verspreid liggen. Natuurk. Verhandelingen der Hollandsche Maatsch. van Wetensch. XIX. Haarlem 1831, p. 341—349.

as in Scandinavia ¹⁾. It is to be noted that on his first geological map these diluvial beds are not marked out in separate divisions ²⁾.

Two years later, however, his attention was arrested by the peculiarity that, while in Twente and in the Eastern part of Salland and probably over the whole extent of the Veluwe, the principal constituents of these erratics were quartzite, red or blackish jasper, near the Havelter hill, before Steenwijk when one comes from the side of Meppel; one suddenly finds the detritus to consist entirely of flints. He noticed the same phenomenon near Steenwijk, the Steenwijkerwold and even near Vollenhove ³⁾. These facts led him to conclude that two distinct diluvial deposits had taken place, i. e. one of "siliceous material" transported from the Baltic and another "composed of quartz" derived from the Ardennes.

In 1854 STARING had modified his theories. To the siliceous formation he gave the name of "Scandinavian Diluvium", and the quartz, which he no longer regarded as derived from the Ardennes, received the appellation of "Diluvium of the Rhine", which also included the deposits between the Meuse and the Rhine; and the beds situated South of the river Lek received the name of Diluvium of the Meuse. He was careful to add however that: "it would be wrong to deduce from these appellations that Scandinavia alone was responsible for the diluvial formation in the North of Holland, and the Ardennes, or the mountains of what at present is known as the basin of the Meuse, for that of one of its Southern parts and the Rhine for that of the other." ⁴⁾

Six years later STARING again proposed another division which he then considered decisive. Leaving the boundaries of the Scandinavian Diluvium and those of the Meuse unaltered, the limits of the diluvium of the Rhine were confined to those parts of the Netherlands lying between the Rhine and the Meuse. The formation North of the Rhine and South of the Vecht was indicated by the name of "mixed diluvium" ⁵⁾, which therefore included the provinces of Overijsel, Guelders, Utrecht, and the district of the Gooi in North Holland. The characteristic feature of this diluvium is the presence of erratics from

¹⁾ De Aardkunde en de Landbouw in Nederland. Zwolle 1844, p. 14.

²⁾ Proef eener geologische kaart van de Nederlanden. Groningen 1844.

³⁾ De Aardkunde van Salland en het Land van Vollenhove. Zwolle 1846, p. 8, 9, 53.

⁴⁾ Het eiland Urk volgens den Hoogleraar HARTING en het Nederlandsche diluvium. Verhandel. uitgegeven door de Commissie belast met het vervaardigen eener geologische kaart van Nederland. II. Haarlem 1854, p. 167 m. kaart.

⁵⁾ De Bodem van Nederland. II. Haarlem 1860, p. 54—56. Pl. I.

Scandinavia, from Hanover, from the mountains along the banks of the Rhine and from the Ardennes; but STARRING was unable accurately to define which erratics had been transported by the Rhine and which by the Meuse.

"By far the largest portion of the quartzites, sandstones, pudding-stones and slates, found in those parts of the diluvium, which are "situated to the South of the Scandinavian drift, are derived from the "Devonian strata of the Rhine and the Ardennes." ¹⁾ Neither did STARRING succeed in proving that the erratics in the diluvium of the Meuse had originally come from the Ardennes. "The gravel and the "flints of the Meuse are similar to those of the Veluwe, with the "important difference, however, that no fragments of plutonic rocks "are found among them." ²⁾

Although for the last ten years the erratics transported from the North of Europe have been the subject of much careful investigation, little interest has been bestowed on those derived from Southern parts. This neglect is due in a great measure to the very nature of those rocks. The first actual proof that detritus from the Ardennes has been carried North of the Rhine, was supplied by J. LORRÉ when he discovered a *Rhynchonella Thurmanni* near Wageningen ³⁾; but until now scarcely any further progress has been made in the study of this question.

The difficulty of tracing to their original home the boulders transported from the Ardennes, lies in the first place in the necessity of leaving out of consideration, fragments of those rocks which are represented both in the diluvium of the Rhine and in that of the Meuse, for it is impossible to determine the exact districts to which they originally belonged. In the second place, it is a well known fact that the greater part of the Ardennes is very poor in fossils, so that the chance of finding fossiliferous specimens among the diluvial erratics is almost nil; — and thirdly, some of the very characteristic rocks, e. g. the phyllites, are much too soft to offer adequate resistance to the accidents of transportation. However, as I hope to show in the following pages sufficient material from various formations

¹⁾ l. c. p. 97.

²⁾ l. c. p. 96.

³⁾ Contributions à la géologie des Pays-Bas. Archives Teyler (2) III. Haarlem 1887, p. 80.

Postscript: FERD. ROEMER has already mentioned silicified specimens of *Stephanoceras coronatum*, found in the boulders near Winterswijk, Guelders. (N. Jahrb. f. Min. 1854, p. 322, 323). These looked exactly like those occurring in the jurassic layers of Northern France. See also Cl. Schlüter in Zeitschr. d. D. geolog. Ges. XLIX. 1897, f. 486.

remains to prove that the erratics traceable to the Ardennes may claim a considerable share in the formation of the mixed diluvium ¹⁾).

Cambrian system. The principal part of the Ardennes is built up of layers belonging to the Cambrian system, which A. DUMONT originally sub-divided into three groups, namely Devillian, Revinian and Salmian ²⁾). The Devillian and Revinian systems were afterwards united by J. GOSSELET, ³⁾ into one series, called the devillo-revinian, which consists of phyllites, alternating with bands of greyish black and dark bluish grey quartzites. These layers may be seen exposed principally near Revin and Deville, on the banks of the Meuse, near Rocroi and Stavelot, and also near Givonne, to the north of Sedan. ⁴⁾ These quartzites are often crossed in various directions by fine veins of quartz and — a distinctive feature by which they are easily recognized — they often contain small cubes of pyrite, which in some cases has been in a greater or lesser degree changed into hydroxyde of iron. Now and then specimens are found in which the original mineral has entirely disappeared, only the impression of the cubes being left. J. DE WINDT ⁵⁾ has given microscopical descriptions of these crystalline quartzites, but has omitted to mention one special characteristic in which they show great conformity with the phyllites. In reference to the latter, E. GEINITZ was the first to point out that the enclosed crystals of magnetite and pyrite are surrounded by a zone of quartz, thus forming elongated lenses. ⁶⁾ From the manner in which these minerals have grown together, as well as the chlorite, he was led to the conclusion that they were coeval. This theory has been refuted by A. RENARD. Although, with GEINITZ, he believes the magnetites and pyrites to have been formed at the same time as the mass of the rocks, he

¹⁾ In all probability this share will be found to be much larger than is thought at present, because a great many rocky fragments, among others quartzites and sandstones, are now ascribed to the diluvium of the Rhine although they are also present in that of the Meuse.

²⁾ Mémoire sur les terrains Ardennais et Rhénan-Mémoires de l'Acad.-roy. de Belgique XX. Bruxelles 1847, p. 8.

³⁾ Esquisse géologique du nord de la France. Lille, 1880, p. 19.

⁴⁾ It cannot be made out which of these localities have provided the boulders. They are represented in the accompanying map as if they were coming from Revin, the chief locality.

⁵⁾ Sur les relations lithologiques entre les roches considérées comme cambriennes des massifs de Rocroi, du Brabant et de Stavelot. Mém. cour. de l'Acad. roy. de Belgique LVI. Bruxelles 1898, p. 21, 68.

⁶⁾ Der Phyllit von Rimognes in den Ardennen. TSCHERMAK's Mineralog. und Petrogr. Mitthlg. III. Wien. 1880, p. 533.

considers the zone of quartz surrounding these minerals to be of secondary origin, and that pressure on both sides had caused cavities which afterwards have been filled up with quartz. ¹⁾ Some time before, A. DAUBRÉE had already furnished a description of transformed crystals of pyrites found near Rimognes. ²⁾ The studies of other kinds of rocks led to the same conclusion. ³⁾ An analysis of the pyritiferous quartzites of the Cambrian system affords still better proof of the secondary origin of this quartz, because in this case the rock itself is composed of this mineral. When examining specimens, it is easy to observe the sharp contrast between the two formations. The quartz which has formed itself around the pyrite, is clear and transparent, seldom contains enclosures, and is built up of fibres which stand perpendicular on the crystals of pyrite. The same structure is seen in the parts which form the veins. L. DE DORDOLOT, who has written on the same subject, is inclined to regard this quartz as chalcedony. ⁴⁾

By the aid of this data it has not been difficult to prove that erratics of this kind have been widely dispersed, and it is very probable that in the course of time their presence will be signalized from many other places besides those we here indicate.

1. Province Utrecht: Railway cutting near Rhenen, on the river Lek, Darthuiser Berg, sandpit to the North of Rijsenburg, railway cutting at Maarn, the heath near the pyramid of Austerlitz, near Zeist, Heidebosch near the House ter Heide, between the stations de Bilt and Zeist, to the rear of Houderinge near de Bilt, Soester Berg.

2. Province of North-Holland: Hilversum and the sandy tract to the North of Larenberg.

3. Province of Guelders: Heath near Epe, Bennekom near Wageningen, Eerbeek near Dieren, at several places around Eibergen Borculo, Groenlo and Hettenheuvel near Doetichem.

4. Province of Overijssel: Heriker Berg near Markelo.

¹⁾ Recherches sur la composition et la structure des phyllades ardennais. Bull. du Musée roy. d'hist. nat. de Belgique. II. Bruxelles 1883, p. 134—135.

²⁾ Etudes synthétiques de géologie expérimentale. I. Paris 1879, p. 443.

³⁾ H. LORETZ. Ueber Transversalschieferung und verwandte Erscheinungen im thüringischen Schiefergebirge. Jahrbuch der k. preuss. geolog. Landesanstalt für 1881. Berlin 1882, p. 283—289.

HANS REUSCH. Bömmelöen og Karmöen met omgivelser. Kristiania 1888, p. 69, 70.

ALFR. HARKER. On "Eyes" of Pyrites and other Minerals in Slate. Geolog. Magazine (3) VI. London 1889, p. 396, 397.

⁴⁾ Quelques observations sur les cubes de pyrite des quartzites reviniens. Ann. Soc. géolog. de Belgique. XXXI. Liège 1903—04. Mém. p. 505.

It stands to reason that erratics of this type must be more plentiful still in the district South of the Rhine; in fact, similar quartzites have been found in the diluvium of the Meuse for a long time past. In the Province of Limburg they are looked upon as the most common kind of erratics. ALPH. ERENS came across one 3 M. high, 2.6 M. long and 0.6 M. broad ¹⁾. According to this author, they are also found in quantities in the Province of North Brabant, although they are not so large as those of Limburg. J. LORIÉ found rocks of this composition on the heaths at Mook and at Schaik, also in South Holland on the beach of Springer in Goedereede and near Rockanje in the island of Voorne.

“Porphyroids.” But the most conclusive proofs that immense quantities of rocky fragments must have been transported from the Ardennes, are furnished by the so-called Porphyroids. This rocky formation is confined to the districts of Revin and Deville, where, more particularly in the neighbourhood of Laifour and Mairus, they form dikes from 0.1 to 20 M. wide, corresponding to the layers of the devillo-revinian group. At present only 17 places are known where this exceedingly characteristic formation ²⁾ may be encountered. Dispersed in a bluish gray or greyish groundmass, may be seen porphyritic crystals of bluish quartz and of feldspar. Owing to their peculiar position and their schistose structure, many geologists have classified these rocks among the series of crystalline schists, — whilst others have ascribed to them an eruptive origin. CH. DE LA VALLÉE POUSSIN and A. RENARD, who have given the most detailed description of these rocks, favoured the former view ³⁾; BARROIS, DAUBRÉE, GOSSELET, VON LASAULX and others, on the contrary, justly considered them to be quartzporphyry, an opinion which A. RENARD also finally accepted.

Although these porphyroids can have but a minimum share in the formation of the Ardennes, they are frequently met with in diluvial deposits. In Belgium, G. DEWALQUE only noticed them near Liege ⁴⁾, which proves that but little attention has been paid to them in that

¹⁾ Recherches sur les formations diluviennes du sud des Pays-Bas. Archives Teyler (2) III. 6ème partie. Haarlem 1891, p. 23.

²⁾ J. GOSSELET. L'Ardenne. Paris 1888, p. 86.

³⁾ Mémoire sur les caractères minéralogiques et stratigraphiques des roches dites plutoniques de la Belgique. Mémoires cour. etc. de l'Acad. roy. de Belgique XL. Bruxelles 1876, p. 237—247 (also Zeitschr. d. D. geol. Ges. 1876, p. 750—769).

⁴⁾ Prodrome d'une description géologique de la Belgique. Bruxelles et Liège 1868, p. 237.

country ¹⁾, for ALPH. ERENS mentions not less than 15 gravel-pits in the neighbourhood of Maastricht in which he found fragments of these rocks, one being 0.6 M. long and 0.5 M. thick. The most easterly place of deposit known at present is Simpelveld ²⁾. Not long ago, Mr. L. RUTTEN brought me several specimens dug up in the neighbourhood of Sittard. From observations of ERENS, it would appear that these erratics are scarce in the Province of North Brabant. He himself found a nice piece at Mook ³⁾, and J. LORIÉ a fragment between Bladel and Postel.

North of the Rhine they have been discovered in the railway cuttings near Rhenen and also near Maarn (in the latter locality the fragment was over $\frac{1}{2}$ M. in diameter), and on the Soester Berg, in the Province of Utrecht. Another piece was found near Eibergen, in Guelders and finally ERENS mentions having seen in the Geological Museum, at Leiden, a fragment found in Overijssel: unfortunately he does not state the exact spot at which it was found ⁴⁾.

2. *Carboniferous system.* FERD. ROEMER has given a description of a few fragments of black carboniferous limestones containing *Productus striatus* Fisch. found in the Gooi, near Hilversum and sent to him for analysis by STARING. He came to the conclusion that they were derived from the carboniferous limestone of the district between Aix-la-Chapelle and Stolberg ⁵⁾.

STARING on the contrary believed them to have been transported from Visé on the Meuse, in Belgium, and based his opinion on the similarity of their composition with the limestone found in that part and also on the almost total absence of this rock from Westphalia. ⁶⁾ Although fragments of carboniferous limestone from Ratingen, N.W. of Dusseldorf, might have found their way to the Netherlands, the fact that no traces of the said fossil have ever been observed in those rocks ⁷⁾, evidently keeps them outside the discussion. It is true that in the district between Aix-la-Chapelle and Stolberg, the

¹⁾ J. LORIÉ e.g. found several fragments near Lancklaer on the Zuid-Willemskanaal.

²⁾ Note sur les roches cristallines recueillies dans les dépôts de transport dans la partie méridionale du Limbourg hollandais. Ann. de la Soc. géolog. de Belgique. XVI. 1888—89. Liège. Mém. p. 417—420.

³⁾ Recherches sur les formations diluviennes du sud des Pays-Bas. Archives Teyler (2) III. 6^{ème} partie. Haarlem 1891. p. 23, 33.

⁴⁾ Recherches sur les formations diluviennes. l. c. p. 67.

⁵⁾ Ueber Holländische Diluvial-Geschiebe. Neues Jahrb. f. Mineralogie. 1857, p. 389.

⁶⁾ De Bodem van Nederland. II. Haarlem 1860, p. 96.

⁷⁾ H. von DECHEN. Erläuterungen zur geologischen Karte des Rheinlandes und der Provinz Westfalen. II. Bonn 1884, p. 216.

Productus striatus is occasionally met with ¹⁾, but, like many other fossils, it is extremely rare. ²⁾ The probability of one of these specimens having been transported to the Gooi becomes therefore nil. On the other hand, as STARING had already pointed out, they are very common at Visé in Belgium, consequently we are justified in concluding that the above mentioned fragments must be referred to that locality.

Other fossil mentioned by ROEMER is the *Goniatites sphaericus* Mart. (*Glyphioceras sphaericum*), a specimen of which had been found near Holten, in Overijssel, and whose original birth-place he claims to have been the valley of the Roer. This fossil, however, is found both at Ratingen and Visé: nothing definite can therefore be said with regard to the place of its origin. I may here mention that in 1899, Dr. E. COLLINS brought me a fine specimen, well preserved and but little polished, which had been picked up in the gravel of a garden at Utrecht and was very probably brought from the Lek.

In the railway cutting near Maarn, to the East of Driebergen, I found in 1893 a block of crinoidal limestone weighing as much as 97 K.G. In that same cutting repeatedly were observed pieces of compact black limestone. In 1895, fragments of a very beautiful crinoidal limestone were found in the grounds of the villa Houderinge, near De Bilt, at a depth of about 1 M. Other pieces of black and next to these of grayish compact limestone were found in a railway cutting half way between the stations of De Bilt and Soest. On the whole, therefore, it cannot be said that rocks of this type are largely represented in the diluvial deposits under consideration. This is probably owing in a large measure to the sandy nature of the diluvium of those parts which allows the moisture of the atmosphere to penetrate to the limestone and gradually dissolve it. The same physical conditions are probably also responsible for the paucity of erratics of this description in the Provinces of North-Brabant and Limburg, and in the Campine. A. ERENS found fragments of crinoidal limestone near Oudenbosch, ⁴⁾ É. DELVAUX of carboni-

¹⁾ H. VON DECHEN. l. c. p. 211.

²⁾ C. DANTZ did not even come across a single specimen in the district of Aix-la-Chapelle. (*Der Kohlenkalk in der Umgebung von Aachen. Zeitschr. d. D. geolog. Ges.* XLV. Berlin 1893. p. 611).

³⁾ L. G. DE KONINCK. *Recherches sur les animaux fossiles. 1^{ère} partie. Monographie des genres Productus et Chonetes.* Liège 1847. p. 30.

⁴⁾ *Recherches sur les formations diluviennes* l. c. p. 67.

ferous limestone in a gravel pit at Gelieren near Genck.¹⁾ and J. LORIE at Smeermaes and Lancklaer, on the Zuid-Willems canal.

The original home of these various limestones cannot be determined with any certainty. However, as numerous layers of crinoidal limestone are present in the districts of Aix-la-Chapelle and Stolberg²⁾ as well as in the valley of the Meuse, more especially near Dinant, it seems rational that we should in the first place look to these parts for their origin³⁾. In any case they must have been transported along the Meuse, for the district Aix-la-Chapelle—Stolberg is drained by the Geul, the Inde and the Worm, which all three flow into the Meuse.

Finally ROEMER gives in his treatise a description of fragments of plithanite, found near Ootmarsum, in Overijssel, which he thinks derived from the layers of culm on the lower Rhine. This conjecture is not inadmissible, but at the same time the fact must not be overlooked that this kind of rock is also plentiful in the valley of the Meuse.

Jurassic System (Oxfordian). In the foregoing pages mention has already been made of a piece of brownish yellow sandy clay, found by J. LORIE on the Wageningen hill (Guelders) in which was imbedded a perfect specimen of *Rhynchonella Thurmanni* Voltz, in every respect similar to the fossils of this species found at Vieil-Saint-Rémy, to the South-West of Mézières in the department of the Ardennes⁴⁾. This is the only fossil of this type discovered in our country, although in the diluvium of South Limbourg and Northern Belgium, jurassic

¹⁾ Les anciens dépôts de transport de la Meuse, appartenant à l'assise moséenne observés dans les ballastières de Gelieren près Genck en Campine. Ann. Soc. géol. de Belgique XIV. 1886—87. Liège 1887, Mém. p. 103.

Here again, as at Maarn, he ascribed their presence to an "accident".

²⁾ J. BEISSEL. Ueber Struktur und Zusammensetzung des Kohlenkalks in der Umgebung von Aachen. Verhandl. naturh. Vereins Rheinl. u. Westf. XXXIX. Bonn 1882. Corresp. Bl. p. 92.

³⁾ ED. DUPONT. Notice sur les gîtes de fossiles du calcaire des bandes carbonifères de Flourens et de Dinant. Bull. Acad. roy. de Belgique (2) XII Bruxelles 1861 p. 293.

ED. DUPONT. Essai d'une carte géologique des environs de Dinant l. c. (2) XX. 1865. p. 621, 622, 629.

ED. DUPONT. Carte géologique des environs de Dinant. Bull. Soc. géol. de Fr. (2) XXIV. Paris 1866—67 p. 672, 673.

ED. DUPONT et MICHEL MOURLON, Explication de la feuille de Dinant. Musée d'hist. nat. de Belgique. Service de la carte géolog. du Royaume. Bruxelles 1883, p. 9, 26, 33, 34, 53 et passim.

⁴⁾ Contributions à la géologie des Pays-Bas. Archives Teyler (2) III. Haarlem 1887, p. 10.

fossils have been frequently met with. We find them already mentioned by J. T. BINKHORST VAN DEN BINKHORST ¹⁾.

FR. SEGHERS discovered a Rhynchonella and part of an Ammonites at Genck ²⁾. Close to this place, at Gelieren, E. DELVAUX frequently came across remains of "calcaire à Chailles" ³⁾. C. MALAISE gave a description of petrified Nerinea found at Rothem and an Isastraea at Jambes, near Namur ⁴⁾. A. ERENS mentions a few other fossils ⁵⁾ and finally we have an account of a yellow oolite, discovered by E. VAN DEN BROECK among the erratics of the Meuse, and here we call attention to the peculiar siliceous oolites scattered about the plateau of the Meuse and which probably belong to the jurassic system ⁶⁾. As yet no trace of similar oolites has been discovered North of the Rhine, but J. LORÉ noticed some in the borings of a well at Mariendaal, near Grave ⁷⁾. A few weeks ago Mr. L. RUTTEN found a small pebble in the diluvium at Kollenberg, near Sittard.

Tertiary system. (Eocene). Very interesting are the accounts of the discovery of erratics comprising specimens of *Nummulina laevigata* Lam. FERD. ROEMER has given a description of a fragment of this kind derived from Holten, in Overijssel, but believed it to have only accidentally found its way among the erratics ⁸⁾. STARING made mention of a couple of rounded-off pieces of hornstone, one of which had been found on the rising ground of Hellendoorn and the other on the Steenshul, near Oldebroek, and which he referred to the Alps? "If we did not know the place where these specimens were obtained, "we should be rather inclined to think they came from a collection "in which the objects had been confused and believe these rocks to

¹⁾ Esquisse géologique et paléontologique des couches crétacées du Limbourg. Maastricht 1859. p. 7.

²⁾ Ann. de la Soc. malacolog. de Belgique X. Bruxelles 1875. Bull. p. XXXIV.

³⁾ Les anciens dépôts de transport de la Meuse, appartenant à l'assise moséenne observés dans les ballastières de Gelieren près Genck en Campine. Bull. Soc. géolog. de Belgique XIV. 1886/87. Liège. 1887. Mém. p. 102.

⁴⁾ Sur quelques fossiles du diluvium. Ann. Soc. malacolog. de Belgique X. Bruxelles 1875. Bull. p. IV.

⁵⁾ Note sur les roches cristallines l. c. p. 413.

⁶⁾ E. VAN DEN BROECK. Les cailloux oolithiques des graviers tertiaires des hauts plateaux de la Meuse. Bull. Soc. belge de Géologie III. Bruxelles 1890 p. 404—412.

X. STAINIER. Origine des cailloux oolithiques des couches à cailloux blancs du bassin de la Meuse. Ann. Soc. géolog. de Belgique XVIII. 1890—92, p. CV, 92.

E. VAN DEN BROECK. Coup d'oeil synthétique sur l'Oligocène belge. Bull. Soc. belge de Géologie VII. Bruxelles 1893 p. 25, 266.

⁷⁾ Beschrijving van eenige nieuwe grondboringen, Verhandel. K. Akademie v. W. 2de sectie. VI, N. 6. Amsterdam 1899, p. 33.

⁸⁾ Ueber Holländische Diluvial-Geschiebe. Neues Jahrb. f. Min. 1857, p. 392.

"have been picked up near Brussels ¹⁾". K. MARTIN ²⁾ and J. LORIE ³⁾ in fact assign them also to that locality; they forget, however, that no strata of nummulitic limestone are known to exist there ⁴⁾. Their origin lies much farther South. In 1863 J. GOSSELET had already indicated the original source of these "silex à Nummulites", of which a few years later he published a description ⁵⁾. They are dispersed in large quantities in the arrondissement of Avesnes, in the department du Nord, more especially in the environs of Trélon ⁶⁾ where, on account of their hardness, they are frequently used for the paving of roads.

Since then numerous fragments of this rock have also been found in Belgium, specially on the plateau situated between the Meuse and the Sambre, e. g. around Silenrieux, Sivry, Clermont, etc., as well as in parts lying further West ⁷⁾.

The second question which we have to examine, is the period at which these rocky fragments from the Ardennes have been transported to districts at present situated North of the Rhine. The view expressed by STARRING that this transport has taken place before the deposition of Scandinavian erratics, seems at present also satisfactorily established, for those carried by the Meuse. In the railway cuttings at Maarn and Rhenen, rocks of diverse origin lie together in friendly

¹⁾ De Bodem van Nederland. II. Haarlem 1860, p. 89.

²⁾ Niederländische und Nordwestdeutsche Sedimentärgeschiebe. Leiden 1878, p. 37.

³⁾ Les métamorphoses de l'Escaut et de la Meuse. Bull. Soc. belge de Géologie, IX. 1895 Bruxelles 1895—96, Mém. p. 60.

⁴⁾ E. VAN DEN BROECK. A propos de l'origine des Nummulites laevigata du gravier de base du Laekénien. Bull. Soc. belge de Géologie. XVI. 1902. p. 580.

⁵⁾ De l'extension des couches à Nummulites laevigata dans le nord de la France. Bull. Soc. géolog. de la France (3) II. 1873—74. Paris 1874, p. 51—58. See also Ann. Soc. géol. du Nord. I. 1870—74. Lille, p. 36.

⁶⁾ Compte-rendu de l'excursion du 7 Septembre [1874] à Trélon l. c. p. 681. Leriche. L'Eocène des environs de Trélon. Ann. Soc. géol. du Nord. XXXII. Lille 1903. p. 179.

⁷⁾ MICHEL MOURLON. Sur les amas de sable et les blocs de grès dissiminés à la surface des collines famenniennes dans l'Entre-Sambre-et-Meuse. Bull. Acad. roy. de Belgique (3) VII. Bruxelles 1884, p. 301—303.

A. RUTOT. Sur l'âge de grès de Fayat. Bull. Soc. belge de Géologie I, 1887, p. 47.

L. BAYET. Première note sur quelques dépôts tertiaires de l'Entre-Sambre-et-Meuse. Bull. Soc. belge de Géologie X, 1896. Bruxelles 1897—99 p. 139—140.

G. VELGE. De l'extension des sables éocènes laekéniens à travers la Hesbaye et la Haute Belgique. Ann. Soc. géolog. de Belgique, XXV, 1897—98. Liège, p. CLXV.

A. BRIART. Notice descriptive des terrains tertiaires et crétacés de l'Entre-Sambre-et-Meuse. Ann. Soc. géolog. de Belgique XV. 1887—88, p. 17.

juxtaposition and intermixture, which proves that they must have been carried together and at the same time to the place where they are found at present. From the shape of the front moraine, we conclude that the direction of the transport was from the North-East. The erratics nowadays found at the surface have been gradually denuded by the action of water and wind. It is therefore evident that originally these erratics were transported much farther to the North and East, than their present place of deposit, because they were seized by the advancing Baltic icestream and carried along together with the material of its moraine. We are therefore justified in fixing the period of the transport of the boulders from the Rhine and Meuse at the commencement of the epoch of maximum glaciation (Saxonian).

A far greater difficulty presents itself when we attempt to determine in what way this transport has taken place, for it can only have been effected by the agency of a river or a glacier. The hypothesis that all these boulders should have been carried along by the Meuse in its downward course, is scarcely admissible. Even leaving out of account the finding of rocky fragments from the Ardennes on the strands of Goedereede and Voorne — not to speak of Suffolk, in England — there remains a large tract of land 105 K.M. long stretching from Utrecht to Eibergen, over which these erratics are dispersed in the shape of a crescent. If carried by the Meuse, its mouths must have extended over a very large area. But a greater objection to this theory is that, in that case, they must have been transported across the Rhine (at present the IJssel) because rocks of this kind are found at places to the East of this river (Doetichem, Eibergen, Markelo). Finally, some of these blocks are so large that they could not possibly have been transported by a river. Besides, some of them present no marks of polish, which is another argument against their transport by running water.

For the better understanding of these objections we quote a few examples from the Province of Limburg and the Campine. A. ERENS found in the environs of Maastricht numerous large blocks of Cambrian quartzites, one of which was 3 M. high, 2,6 M. long and 0,6 M. in width, computed to weigh about 12400 K.G. ¹⁾ More important still are the blocks of sandstone found in the diluvium of the Campine at Holsteen-Molenheide, near Zonhoven, in the neighbourhood of Hasselt, É. DELVAUX noticed blocks measuring from 4

¹⁾ Note sur les roches cristallines l. c. p. 412, 417. Mr. L. RUTTEN informed me that in the neighbourhood of Sittard similar boulders reach a diameter of ± 3 M.

to 36 M. cub, weighing from 10600 to 95400 K.G. ¹⁾). He believed them to belong to the landenian stage of the eocene system. His opinion, that they covered the plateau of the Ardennes (where CH. BARROIS was the first to discover similar masses ²⁾), to a height of 672 M., has been much contested. E. VAN DEN BROECK classed these sandstones first among the triassic system ³⁾, afterward referred them to the oligocene system ⁴⁾, and finally suggested they might either be oligocene, miocene or pliocene, but certainly not eocene ⁵⁾. G. DEWALQUE pronounced them to be miocene ⁶⁾, whilst O. VAN ERTBORN sought their origin in the pliocene system ⁷⁾, more especially in the diestian group ⁸⁾, but was of opinion that they must be regarded as the remains of a "delta caillouteux" ⁹⁾. M. MOURLON, on the contrary, held that they had been formed in the vicinity of their present place of deposit, by the fusion of the "sable de Moll" ¹⁰⁾, an opinion which cannot be maintained, because similar blocks are present in the diluvium of Maastricht where no trace of this sand exists ¹¹⁾.

J. GOSSELET compares these rocks with the freshwater-quartzites of the diluvium of the Rhine and, with reason, thinks that they belong to the oligocene system ¹²⁾. At all events it is universally admitted that the Ardennes have been covered by extensive layers of tertiary

¹⁾ Description sommaire des blocs colossaux de grès blanc cristallins provenant de l'étage landénien supérieur en différents points de la Campine limbourgeoise. Ann. Soc. géolog. de Belgique XIV. 1886—87. Liège 1887. Mém. p. 117—130.

²⁾ Sur l'étendue du système tertiaire inférieur dans les Ardennes. Ann. Soc. géol. du Nord. VI. Lille 1879, p. 371.

³⁾ Ann. Soc. roy. malacolog. de Belgique XVI. Bruxelles 1880. Bull. p. LXXIV.

⁴⁾ Note préliminaire sur le niveau stratigraphique de la Belgique et de la région d'origine de certains des blocs de grès quartzeux de la Moyenne et de la Basse-Belgique. Bull. Soc. belge de Géologie IX. 1895. Bruxelles Proc. verb. p. 94—99.

⁵⁾ Les grès erratiques du sud du Démer et dans la région de HEURCK. Bull. Soc. belge de Géologie XV. 1901. Bruxelles 1902. Proc. verb. p. 628.

⁶⁾ Ann. Soc. géolog. de Belgique. XIV. 1886—87. Liège 1887. Bull. p. 18.

⁷⁾ Le Quaternaire dans le sud de la Belgique. Bull. Soc. belge de Géolog. XV. 1901. Proc. verb. p. 662.

⁸⁾ Quelques mots au sujet des divers niveaux gréseux du tertiaire supérieur dans le nord de la Belgique. l. c. p. 632.

⁹⁾ Contribution à l'Étude des Étages rupélien, boldérien, diestien et poederlien, l. c. XVI. 1902. Mém. p. 65.

¹⁰⁾ Compte rendu de l'excursion géologique en Campine les 23, 24 et 25 septembre. l. c. XIII. 1899. Mém. p. 205, 213, 214.

¹¹⁾ ALPH. ERENS. Note sur les roches cristallines l. c. Pl. XIII.

¹²⁾ L'Ardenne. Paris 1888, p. 833.

system, as has been pointed out by M. LOHEST ¹⁾, X. STAINIER ²⁾, J. CORNET ³⁾ and others.

Before stating our reasons for supposing the presence of a glacier in the Ardennes during the second glacial period, we are willing to admit that J. GOSSELET, who of all geologists knew most of this mountain range, remarked in reference to this hypothesis: "on n'en trouve aucun indice sérieux" ⁴⁾. Indeed we have but few indications in support of it. The first to draw attention to this question was FR. VAN HOREN, who at the time of the making of the railway line between Tirlemont and Jodoigne, found near Bost blocks of quartzites from the Ardennes which presented marks quite similar to the striae caused by glaciers. VAN HOREN, however, did not feel justified in drawing from this discovery the conclusion of the former existence of a glacier ⁵⁾. A year later C. MALAISE observed similar marks on blocks of quartzites on the banks of the Grande Geete, close to the spot formerly occupied by the Abbey of Ramez-les-Jochelette, about 10 K.M. from Bost ⁶⁾. G. DEWALQUE believed to have seen unmistakable striae on blocks of quartzites in the valley of the Amblève, near Stavelot, on the "Hohe Venn" ⁷⁾. E. DELVAUX also noticed these horizontally parallel scratches, but believes them to have been produced by a "torrent entraînant et roulant pêle-mêle des sables et des cailloux." ⁸⁾.

Finally, South of Stavelot, on the road to Somagne, G. DEWALQUE discovered giants' kettles formed by the agency of glaciers ⁹⁾. It is regrettable to find that the more detailed study of this subject has been much impeded by the practice in Belgium of giving the name

¹⁾ Les dépôts tertiaires de la haute Belgique. Ann. Soc. géolog. de Belgique XV. Liège 1887—88. Mém. p. 59.

²⁾ Le grès blanc de Maizeroul. Ann. Soc. géolog. de Belgique XVIII. Liège 1890—91. Mém. p. 61.

³⁾ Etude sur l'Évolution des Rivières belges. Ann. Soc. géol. de Belgique XXXI. 1903—04. Mém. p. 317, 355.

⁴⁾ L'Ardenne, p. 843.

⁵⁾ Note sur quelques points relatifs à la géologie des environs de Tirlemont. Bull. Acad. roy. de Belgique (2) XXV. Bruxelles 1868, p. 645, 664; 1 Pl.

⁶⁾ Roches usées avec cannelures de la vallée de la grande Geethe. l. c. (2) XXVII, 1879, p. 682—685.

⁷⁾ Sur la présence de stries glaciaires dans la vallée de l'Amblève. Ann. Soc. géolog. de Belgique. XII. 1884—85. Liège. 1885. Bull. p. 157—158.

⁸⁾ Note succincte sur l'excursion de la Société géologique à Spa, STAVELOT et LAMMERSDORF en août-septembre 1885. Ann. Soc. roy. malacol. de Belgique XX. Bruxelles 1885, Mém. p. 19.

⁹⁾ Marmites de géants près de Stavelot. Ann. Soc. géol. de Belgique. XXV. 1897—98, p. CXXXVIII.

of pseudoglacial to all kinds of bosses and scratches which elsewhere would scarcely be so called, because they do not in the least resemble the striae of glaciers ¹⁾).

This absence of positive characteristics is however easily explained. Leaving alone the fact that as yet no thorough investigation of the subject has been made, the condition of the Ardennes themselves are very unfavorable to research. Its dense forests, fens and heaths make it difficult to reach the surface of the rocks, whose harder layers are only capable of preserving marks. The reason why so few traces are found on the sides of the valleys and on the plateau of the Meuse becomes plain, when we remember that during the period following the receding of the Northern glacier, the waters of the Meuse rose 200 M. above the level of the sea, and not only filled the whole valley but inundated the plateau of the Meuse and thus destroyed the traces left by the glacier.

Of this we find the clearest proofs in the terraces which have retained their boulders. ²⁾ Besides, exactly the same thing happened with the Rhine and its tributaries. The sand and small pebbles carried along by their waters must necessarily have almost entirely obliterated the marks of the glaciers left on the rocks ³⁾).

Striae, however, are not the only evidences of the action of a

¹⁾ X. STAINIER. Stries pseudo-glaciaires en Belgique. Bull. Soc. belge de Géologie X. Bruxelles 1896. Pr. verb. p. 212—216.

E. VAN DEN BROECK. Contributions à l'étude des phénomènes d'altérations dont l'interprétation erronée pourrait faire croire à l'existence de stries glaciaires. l. c. XIII. 1899. Mém. p. 323—334. Pl. XX.

G. SIMOENS. Sur une roche présentant des stries pseudo-glaciaires en Condroz. l. c. Pr. verb. p. 222—223.

²⁾ É. DUPONT et M. MOURLON. Explication de la feuille de Dinant. Bruxelles 1883, p. 100.

A. RUTOR. Résultats de quelques explorations dans le Quaternaire de la Meuse. Bull. Soc. belge de Géologie. XIV. Bruxelles 1900. Pr. verb. p. 259, 260.

X. STAINIER. Le cours de la Meuse depuis l'ère tertiaire l. c. VIII. 1894 Mém. p. 84. Pl. VII.

E. VAN DEN BROECK. Coup d'oeil synthétique sur l'Oligocène belge et les observations sur le Tongrien supérieur du Brabant l. c. VII. 1893, p. 255, 256, 266.

E. VAN DEN BROECK. Exposé sommaire des observations et découvertes stratigraphiques et paléontologiques faites dans les dépôts marins et fluviomarins du Limbourg pendant les années 1880—81. Ann. Soc. roy. malacolog. de Belgique XVI, Bruxelles 1881. Bull. p. CXXV—CXLII.

³⁾ It might be suggested that the transport of these boulders had taken place by means of ice-floes, but Mr. LOHEST has demonstrated in the most positive manner that these ice-masses are incapable of effecting a notable removal. He comes to the conclusion that among the present climatic conditions no explanation can be

glacier and one might reasonably expect to find in the valleys some remains of the wall of moraines. That this is not the case may be accounted for by the supposition that the great Baltic ice-stream has travelled farther south and in its course also destroyed these evidences. As there exists a great diversity of opinion with respect to this forward movement of the ice-stream, it seems necessary here to state what is known of the dispersion of Scandinavian erratics in the Provinces of Limburg and North-Brabant and the Campine.

As long ago as 1778, J. A. DE LUC mentions the discovery of blocks of granite between Postel and Alfen, and also near Lommel and Helchteren ¹⁾. Subsequently, J. J. D'OMALIUS D'HALLOY drew attention to the numerous blocks of granite and other fragments of "primordial" rocks found on the heath of the Campine. "La quantité de ces blocs doit être été immense; car quoiqu'on fasse un grand usage pour paver les rues, ainsi que pour faire des jetées le long de la mer et des rivières, on en voit beaucoup dans les bruyères". ²⁾ And ENGELSPACH—LARIVIÈRE adds the information that some of these blocks of granite measured several M. cub. ³⁾ Somewhat later again, J. G. S. VAN BREDA mentioned the finding of two pebbles of granite in the subsoil of Maastricht, very justly remarking that these rocks must be regarded of later date than those transported from the Ardennes ⁴⁾. At that time he already spoke of blocks of granite found at Oudenbosch, in North-Brabant ⁵⁾. STARING expressed the opinion that these erratics had been brought there by "some accidental means or other" ⁶⁾, although a short time before NORBERT DE WÆL had recorded the finding, at Weelde, 10 K.M. to the NNE. of Turnhout and also at Poppel,

found for the transport of the blocks of quartzites from the Ardennes. (Sur le transport et le déplacement des cailloux volumineux de l'Amblève. Ann. Soc. géol. de Belgique. XVIII. Liège 1890—91. Bull. p. CVII—CIX).

¹⁾ Lettres physiques et morales sur l'histoire de la terre et de l'homme. IV. Paris et La Haye 1779, p. 54, 57.

²⁾ Mémoires pour servir à la description géologique des Pays-Bas, de la Flandre et de quelques contrées voisines. Namur. 1828, p. 204, 205.

³⁾ Considérations sur les blocs erratiques et roches primordiales Bruxelles. 1829 (fide P. COGELS. Ann. Soc. roy. malacolog. de Belgique. XVI. 1881, Bull. p. LIV).

⁴⁾ Natuurk. Verhandel. van de Holl. Maatsch. v. Wetensch. XIX. Haarlem 1831, p. 390.

⁵⁾ The biggest one originally weighed ± 5300 K.G. (V. BECKER). Het zwerfblok van Oudenbosch en zijne omgeving. Studiën op Godsdienstig, Wetensch. en Letterk. Gebied. XXX. Utrecht. 1888, p. 25).

⁶⁾ De bodem van Nederland II. Haarlem 1860, p. 78.

half-way between the last-named place and Tilburg, of erratics one of which weighed 200 K.G. ¹⁾. G. DELWAQUE then again mentioned two pebbles of granite found in the neighbourhood of Maastricht ²⁾. It is only during the last ten years that a deeper interest has been taken in the study of this subject, with the result that the presence of erratics of Northern origin has been ascertained in several places, as we gather from the writings of C. BAMPs, V. BECKER, E. VAN DEN BROECK, P. COGELS, É. DELVAUX, G. DEWALQUE, A. ERENS, O. VAN ERTBORN, J. LORIE, A. RENARD and CH. DE LA VALLÉE—POUSSIN.

Another fact worthy of notice is the presence, at these very places, of boulders derived from the district of the Rhine. The first indications of such finds, by G. DEWALQUE, are rather questionable. They were fragments of rocks from the lava of Niedermendig, near Andernach, frequently met with in the valley of the Amblève, but were believed to have been fragments of mill-stones, formerly used at Stavelot and Malmedy. Subsequently É. DELVAUX found a few pieces of lava and pumice stone in the diluvium of the Campine ³⁾; but it was A. ERENS who discovered and described a great number of rocks derived from the Rhine district, composed of lava from Niedermendig, pumice stone and Taunus-quartzite ⁴⁾. These were followed at a later period by trachyte from the Drachenfels, basalt and hornblende-andesite from the Siebengebirge, and melaphyre and agate from the basin of the Nahe ⁵⁾. The discovery of these fragments in the North of Limburg admits of no other interpretation than that these rocks must have been carried South, simultaneously with the detritus from Scandinavia.

It cannot be denied that fewer erratics from Scandinavian rocks are found South of the Rhine than North of it. We give the following reasons in explanation of this fact: 1st. During the progress of the Baltic icestream in a South-Western direction, the Scandinavian drift must already have lost a certain portion of its material by the mixture of the debris of its own moraine with that of other sources; 2nd. It must have suffered further loss by mixing with the moraine

¹⁾ Bull. Soc. paléontolog. Bruxelles p. 36. (Séance du 5 Septembre 1858).

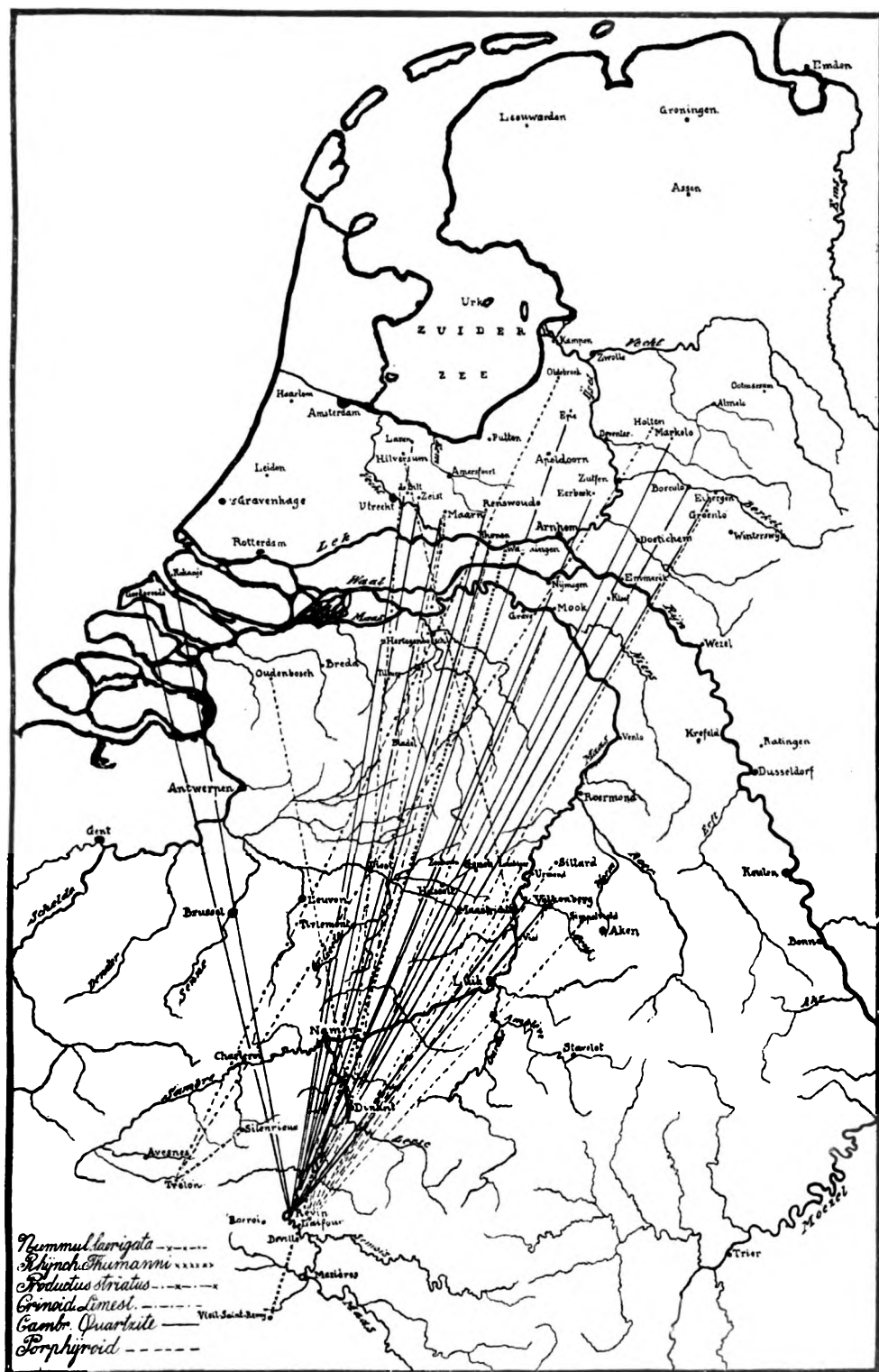
²⁾ Prodrôme d'une description géologique de la Belgique. Bruxelles et Liège. 1868, p. 237.

³⁾ Les anciens dépôts de transport de la Meuse. Ann. Soc. géol. de Belgique XIV. 1886—87. Mém. p. 102.

⁴⁾ Note sur les roches cristallines ... Ann. Soc. géol. de Belgique XVI. 1888—89. Mém. p. 414, 439—441, 444.

⁵⁾ Recherches sur les formations diluviennes du sud des Pays-Bas. Archives Teyler (2) III. 6^{ème} partie. Haarlem 1891. Tableaux synoptiques I—V.

A. WICHMANN. "On fragments of rocks from the Ardennes found in the Diluvium of the Netherlands North of the Rhine."



débris of the glacier from the Ardennes; 3rd. The melting process commenced soon after reaching its Southern limit. It was only during its receding course that the Baltic ice-stream remained for some time stationary, and in this period of inaction was formed the front moraine extending from the South coast of the Zuiderzee to Grebbe and further as shown by J. LORIÉ¹⁾, over Nimeguen to Crefeld. The glacierformations, at present situated South of the Rhine, were afterwards, i. e., during the inter-glacial period, exposed to the turbulent waters of the Meuse, which, as has been stated above, rose 200 M. above the level of the sea, at least between Namur and Dinant, — proof of which is afforded by the high terrace. Although this terrace slopes down towards the North, near Nimeguen, it still reaches a height of between 50 and 100 M. + A.P.²⁾. Owing to this action of the Meuse, the erratics found in North-Brabant and Limburg are generally smaller and more polished than those of the diluvial deposits North of the Rhine. And lastly, a great portion of the glacier formation has got hidden from view by the large alluvial tract of the Rhine delta, which has been formed after the breach of this river at Nimeguen and subsequent alterations of the level by dislocations.

Anyhow, it is entirely out of the question to admit that in the beginning of the quarternary period the Meuse had its outlet into the sea, a little North of Maastricht and formed there an estuary, — a theory put forwards by M. MOURLON³⁾ and A. RUTOT⁴⁾. As J. LORIÉ justly observes, not a single indication exists of the sea having extended so far inland.

1) J. LORIÉ. Le Rhin et le glacier scandinave quaternaire. Bull. Soc. belge de Géologie XVI. 1902. Mém. p. 129—153. N. VIII.

2) l. c. p. 131. The high terrace of the valley of the Meuse is generally considered of pliocene formation, but the presence of Scandinavian erratics in places situated farther North, e. g. Mook, Nimeguen, etc., proves that it must have been formed after the receding of the Baltic ice-stream.

3) Les mers quaternaires en Belgique. Bull. Acad. roy. de Belgique (3) XXXII. Bruxelles 1896 p. 671—711. La faune marine du quaternaire moséen révélée par les sondages de STRYBEEK (Meerle) et de WORTEL, près de HOOGSTRAETEN en Campine. l. c. (3) XXXIII. 1897, p. 776—782.

4) Les origines du quaternaire de la Belgique. Bull. Soc. belge de Géologie. XI. Bruxelles 1897, p. 117.

5) De hoogvenen en de gedaantewisseling der Maas in Noord-Brabant en Limburg. Verhand. K. Akad. van W. Tweede Sectie III. No. 7. Amsterdam 1894, p. 10.

Chemistry. — "*The boiling points of saturated solutions in binary systems in which a compound occurs*". By Prof. H. W. BAKHUIS ROOZEBOOM.

(Communicated in the meeting of November 25, 1905).

In a previous communication ¹⁾ it has been ascertained what branches in the three-phase lines for solid, liquid and vapour may occur in binary systems in which a solid compound appears, namely for the three cases that:

- a. the vapour pressure of the liquid mixtures diminishes gradually from the component *A* to the component *B*;
- b. liquid mixtures occur with a minimum pressure;
- c. liquid mixtures occur with a maximum pressure.

For the right understanding of the behaviour of such systems it is particularly desirable to ascertain what is the order of the phenomena which appear with different mixing proportions of the components when these, at a constant pressure, are brought from low to high temperatures.

If those pressures are very low the mixtures, at a sufficiently low temperature, are completely solid, and on elevation of the temperature, they pass gradually and, at last, completely into vapour, therefore simply a sublimation occurs.

If the pressures are sufficiently high (in the case of components which are not too volatile, 1 atm. is quite sufficient), the solid substances pass gradually and, at last, completely into liquid and these liquids evaporate at still higher temperatures. In this case, fusion takes place first and evaporation afterwards.

With moderate pressures, however, the melting and evaporation phenomena partly coincide, namely when pressures are chosen which occur on the three-phase lines of the components or the compound.

What cases may be distinguished when no solid compound appears has been fully investigated previously, by me. ²⁾

Particular attention has been called to the fact that the three-phase line of the component *B* may be sometimes intersected twice at the same pressure, which is possible when this line exhibits the branches *Ia* and *Ib*, described in the previous communication. (See line *BD* in fig. 1 and 6). In such a case two separate boiling

¹⁾ These Proc. VIII, p. 455. I learned that Dr. SMITS had also come to the conclusion that the minimum on the three-phase line did not coincide with point *H*.

²⁾ Heterogene Gleichgewichte. Heft 2. p. 338, et seq.

points of solutions saturated with solid B occur, one on branch $1b$ and another on branch $1a$. At the last point, boiling does not take place on heating but on cooling. The t, x -figures at a constant pressure have been deduced by me, and the phenomena, in solutions of salts in water and of sulphur in carbon disulphide, have been demonstrated by SMITS and DE KOCK.

The figures 1, 3, 5, 6 show at once that this same case may also occur in solutions saturated with a compound of the two components as soon as their three-phase line shows branch $1b$ as well as $1a$. Examples of two boiling points of the saturated solution have not thus far been noticed in binary compounds although they should be far from rare.

In compounds where, among the saturated solutions, there is present one with a minimum pressure (Fig. 3), a second boiling point of the saturated solution might occur with solutions either richer in A or in B ; in fact a third boiling point at the side of the solution richer in B would be possible if the point D in fig. 3 were situated so low that, at the same pressure, the branches DT_1 , T_1T_2 and T_2H could be intersected in succession. The saturated solution would then in succession first disappear, then reappear to finally disappear once more. Examples belonging to this case have thus far not been sufficiently studied.

If branch 3 of the three-phase line exists for the solutions richer in B (GD in Fig. 1 and 6, GH in Fig. 3 and 5), then if this line is crossed, there occurs at a constant pressure a boiling point of the saturated solution of a different nature from that on branch 1. The t, x -figure of such a case is quite analogous to that derived by me¹⁾ for saturated solutions of the component A whose three-phase line in Fig. 1, 3, 5 always indicates branch 3. On boiling the solution saturated with A the following transformation takes place:



As solid and liquid now pass together into vapour in a definite proportion, it now depends on the quantity of those two phases which of the two disappears at the boiling point. This case occurs for instance on the three-phase line for ice in systems of water and little volatile substances as salts, also on the three-phase line for solid CO_2 in mixtures of CO_2 with less volatile substances such as alcohol.

The same must now also serve for compounds in so far branch 3 occurs therein. Among the binary systems whose liquid-vapour pres-

¹⁾ Heter. Gleichg. II. 341 et seq.

sure always diminishes from *A* to *B*, the branch 3 has thus far only been found with ICl_3 and ICl , as observed in the previous communication. From STORTENBEKER's experiments, it may be deduced that for ICl_3 the branch 3 extends from 34° at 100 mm. to 22.7° at 42 mm., for ICl from 22° at 24 mM. to 8° at 11 mM. The peculiar boiling phenomenon is, therefore, only possible between these temperatures and pressures, but has not been expressly stated in the solutions saturated with ICl_3 or ICl .

In binary systems in which a liquid with a minimum pressure occurs on the three-phase line of the compound, branch 3 must *always* appear as shown in fig. 3 or 5. Among the examples cited in the previous communication, there are sure to be found some where the simultaneous boiling of the solid phase and the solution may take place at 1 atm. pressure.

Another kind of boiling-phenomenon may, finally, take place on branch 2 of the three-phase line of a compound. This branch cannot occur with the components, for the peculiarity of the branch consists in this that the saturated solution contains an excess of the component *B*, whilst the saturated vapour contains an excess of *A*; the compound is, therefore, the phase whose composition is situated between those of the two others. This is, of course, only possible with a compound and not with one of the components.

According to Fig. 1, 3, 5, 6 of the previous communication branch 2 must occur with all compounds where coexisting liquids with an excess of *B* are possible, for it commences immediately at the melting point.

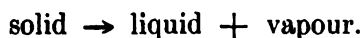
Now, this is possible with a number of hydrated salts which, below their melting point, yield saturated solutions with excess of salt; but the appertaining pressures are then generally so small that the boiling phenomenon cannot be readily observed. In the case of salt-hydrates which occur at a higher temperature so that the equilibrium-pressure on their three-phase line might amount to 1 atm., the solutions richer in salt seem to be very rare and no example is known to me.

An example is, however, known if H_2O is replaced by NH_3 . With the compound $\text{NH}_4\text{Br} \cdot 3\text{NH}_3$, branch 2 appears and the pressures are even greater than 1 atm. In this case the boiling phenomenon has been observed by me.

Branch 2 has, however, been met repeatedly in my previous researches on gas-hydrates where water is then the component *B*. If we now take those hydrates near solutions with more water the

vapour generally contains but little water, and we are dealing with branch 2.

The conversion now taking place with heat supply at a constant pressure is:



In all those cases it is, therefore, not the liquid which boils but the compound. The gas is very plainly seen to emanate from the crystals lying in the liquid, whilst the latter does not diminish but increases. The phenomenon has been very plainly observed with the two hydrates of HCl and of HBr and with those of SO₂ and Cl₂. With the last two and with HCl.H₂O it could be observed at 1 atm. pressure.

It must also exist with ICl but limited between 27° at 39 mm., and 22° at 24 mm., much more plainly with ICl₃ where it may appear between the melting point 101° at 16 atm. and 34° at 100 mm. Between this a three-phase pressure of 760 mm. occurs at 64°, and at the said temperature it may, therefore, be observed in an open apparatus. Solid ICl₃ breaks up into a liquid with 63 and into a vapour with 89 atom-percent of chlorine.

That similar phenomena may also appear in compounds which are very stable at a lower temperature, has recently been demonstrated by ATEN in the case of Bi₂S₃. This sulphide breaks up at 760° into a liquid containing 55 atom-percent of S and a vapour consisting almost exclusively of S. Therefore, the actual melting point of the sulphide cannot be determined at 1 atm. pressure. A similar behaviour may be expected of many compounds having a melting point situated much higher than the boiling point of one of its components, such as in the case of oxides, sulphides, phosphides etc.

We must point out another peculiarity which distinguishes the boiling phenomena on branch 2 from those on branches 1 and 3. The liquids and vapours belonging to the latter are both either richer in A or richer in B than the compound: consequently the boiling phenomena concerned are observed in systems consisting of the compound with a smaller or larger excess of one of the components. On branch 2 however the vapour is richer in A and the liquid richer in B, therefore the boiling phenomenon can occur in mixtures of the compound with A as well as with B. In the first case such a system, below the boiling point at the existing pressure, consists of compound + vapour and the liquid appears only at the boiling point, in the second case, the system below the boiling point consists of compound + liquid and the vapour appears at the boiling

point. In the particular case that the compound was perfectly pure, liquid and vapour should appear both together at the boiling point.

This may be made plain by the example of ICl_3 . The whole t, x -figure at 1 atm. is schematically represented by fig. 7.

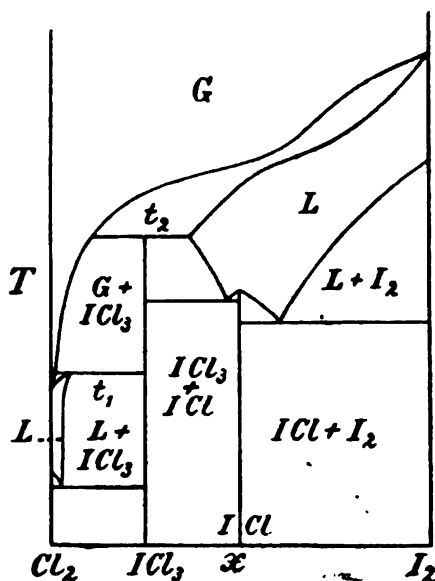


Fig. 7.

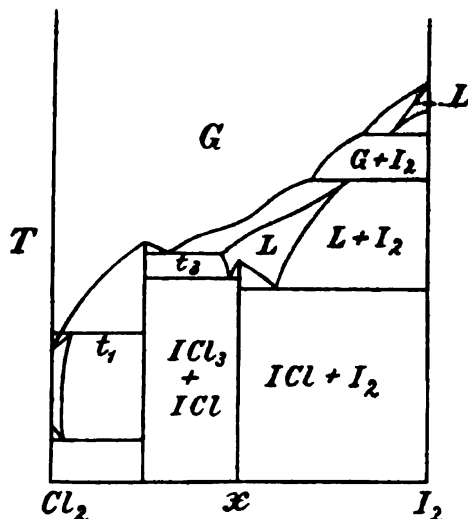


Fig. 8.

in which t_1 represents the temperature (64°) in question. In the different regions G represents vapour and L liquid. The further parts of the figure are entirely dominated in their relative situation by that of the three-phase lines. On this entirely depends which branches of a particular three-phase line will be intersected at the same pressure. In fig. 1 (previous communication) a simultaneous intersection of the branches Ia and Ib is only possible on the three-phase line of the compound. If, however, as with ICl_3 , the melting point F lies at a high pressure, a simultaneous intersection of Ib with 2 or 3 is possible. This is why in Fig. 7, besides the boiling point t_2 on branch 2, t_1 also occurs as boiling point on branch 1b.

The pressure of 1 atm. is also higher for ICl or I than their three-phase line, consequently for these compositions, melting and boiling phenomena occur quite separately and the melting point lines of ICl and I run quite below the boiling point line.

If we take a pressure somewhat lower than 100 mm. we obtain a t, x -figure 8. For ICl_3 we now have again t_1 as boiling point on branch 1b and t_2 as boiling point on branch 3. For ICl , melting and boiling are still quite distinct but at a pressure below 100 mm.

the three-phase line for solid iodine is intersected both on branch 1*b* and 1*a* and therefore the complication in the figure occurs at the side of the iodine.

Still greater complications may appear when according to Fig. 3 (previous communication) there exist liquids with a minimum pressure and when consequently the branches 1*b*, 1*a* and 1*b* can also appear at the side of the liquids richer in *B*, whose intersection at an equal pressure may coincide eventually with those of branch 2 or branch 3. When such systems have been more closely investigated it will not prove difficult to give detailed *t, x*-figures for the same.

Chemistry. — “*The reduction of acraldehyde and some derivatives of s. divinyl glycol (3.4 dihydroxy 1.5 hexadiene)*”. By Prof. P. VAN ROMBURGH and W. VAN DORSEN.

(Communicated in the Meeting of November 25, 1905)

The reduction of acraldehyde (acroleïne) with sodium amalgam ¹⁾ as well as with zinc and hydrochloric acid ²⁾ has been studied by LINNEMANN, who states that he has obtained in the first case propyl and isopropyl alcohol, in the second case isopropyl and allyl alcohol, also a substance called acropinacone of the composition $C_6H_{10}O_2$, or rather a product of non-constant boiling point, of which the fractions boiling between 160°—170° and 170°—180° gave, on analysis, values which led to this formula.

CLAUS ³⁾ could not confirm the results of LINNEMANN as regards the formation of isopropyl alcohol in the reduction with zinc and hydrochloric acid.

GRINER ⁴⁾ has also repeated LINNEMANN's experiments with the object of preparing acropinacone (divinylglycol) but only obtained very small quantities of a liquid without constant boiling point which bore no resemblance to the glycol which, however, was obtained by him in fairly large quantity by reduction of acraldehyde in acetic acid solution with a copper-zinc couple. The other products of the reaction have not been further described by the author.

If we consider the formula of acraldehyde in connection with the

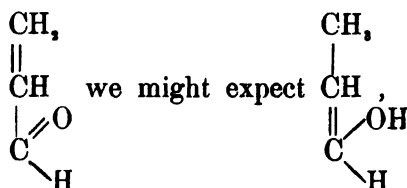
¹⁾ Ann. d. Chem. u. Pharm. **125** (1863) S. 315.

²⁾ Ibid Suppl. III (1864—1865) S. 257.

³⁾ B. B. III. (1870) S. 404. -

⁴⁾ Ann. d. Phys. et Chim. [6] **26** (1892). p. 369.

views of THIELE on the addition of hydrogen to conjugated systems of unsaturated compounds, then on reducing



an unsaturated alcohol which, however, by intramolecular atomic shifting would be converted into $\text{CH}_3\text{—CH}_2\text{—C}\begin{smallmatrix} \text{O} \\ // \\ \text{H} \end{smallmatrix}$, propylaldehyde.

On further reduction this would form propyl alcohol, a substance which actually occurs among the products of the reduction.

Up to the present, propylaldehyde has not been found among the substances formed in the reduction of acraldehyde.

We have, however, succeeded in showing that, although no free propylaldehyde may be present, a derivative of this substance is formed under certain conditions so that the intermediate formation of the said aldehyde is not at all improbable.

First of all the reduction with zinc and hydrochloric acid in ethereal solution according to LINNEMANN has been studied, but we succeeded no more than GRINER in isolating a well defined product — besides allyl alcohol and perhaps smaller quantities of propyl alcohol; generally, the substance obtained, which boiled between $158^\circ\text{—}164^\circ$, contained much chlorine.

If, however, we allow zinc dust to act on a mixture of acraldehyde and glacial acetic acid¹⁾ then, in addition to allyl and propyl alcohol, a neutral liquid is formed (b.p. 170°) from which, after fractionating in vacuo, a product may be obtained boiling between $59^\circ\text{5'—}60^\circ$ at 15 mm. The analysis and the vapour density lead to the formula $\text{C}_3\text{H}_4\text{O}_2$.

The compound is not decomposed by potassium hydroxide; neither sodium nor phosphorus pentachloride have any action; it cannot be benzoylated with benzoyl chloride and pyridine. This sufficiently proves the absence of OH groups.

The said properties, however, render it very probable that the substance is an ether. By dilute acids it is hydrolysed although but slowly. An aldehyde-like odour appears but, as the reaction proceeds, the mass becomes so dark with formation of brownish-black resinous

¹⁾ The action of various reducing agents on acraldehyde has been studied. The results will be published in due course.

products that we have not, as yet, succeeded in isolating well-defined compounds.

Bromine is readily absorbed by it and that in a quantity which points to the presence of two double bonds. If we work with a solution of carbon tetrachloride at a low temperature, but little hydrogen bromide is formed.

From a substance of the formula $C_8H_{14}O$, a great many isomers are, of course, possible. We cannot enter here into a description of the different experiments made in order to elucidate the structure of the product obtained, but we may state that we have finally succeeded by means of a synthesis, which leaves no doubt whatever.

If, on s-divinyl glycol which, thanks to the beautiful researches of GRINER, may be readily prepared, propylaldehyde is allowed to act for 6 days at 90° , a substance is obtained identical with the one described above.

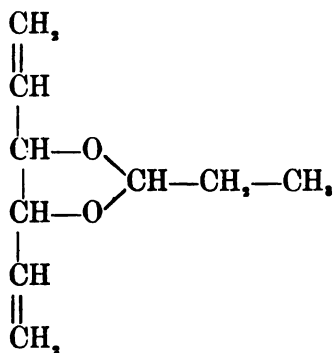
(Sp. gr. at 12° of the synthetic product 0.9392

„ „ „ „ „ „ original „ 0.9416

Refraction at 12° of the synthetic „ 1.4434

„ „ „ „ „ „ original „ 1.4430.)

As to the synthetic product, propylidene s. divinylethylene ether, must be given the formula :



the original must also be considered as a derivative of propylaldehyde. It is, of course, possible that there might be formed at first an analogous acetaldehyde derivative, which afterwards got converted into a propylaldehyde derivative, but considering the comparative difficulty with which the vinyl group combines with hydrogen, this looks less probable.

As one of us (v. R.) explained many years ago, s. divinylglycol or 3.4 dihydroxy 1.5 hexadiene would form an excellent material for the preparation of the hydrocarbon $\text{CH}_2 = \text{CH} - \text{CH} = \text{CH} - \text{CH} = \text{CH}_2$, otherwise hexatriene 1.3.5.

Different methods which we have tried have not led to the desired

end. At last we think we have succeeded by making use of the diformate of s.-divinyl glycol, a compound which may be prepared by heating this glycol for a short time with formic acid.

By fractionating in vacuo, the diformate is obtained as a colourless liquid which at a pressure of 20 mm. boils at 109° and has a sp. gr. of 1.0747 at 11° . A determination of the formic acid (by saponification) gave the amount required for diformate.

In a communication about to follow, the hydrocarbon prepared from the diformate and the method of its preparation will be fully described.

University Org. Chem. Lab. *Utrecht*.

Chemistry. — “*The occurrence of β -amyrine acetate in some varieties of gutta percha*”. By Prof. P. VAN ROMBURGH and N. H. COHEN.
(Communicated in the meeting of November 25, 1905).

Last year, a compound melting at 234° was found by one of us (v. R.) in the gutta percha of *Payena Leerii*¹⁾ of which it could be stated that it is *not* identical with lupeol cinnamate, which occurs in many varieties of gutta percha; the quantity was then too small for further research. Since then a little more of that product was prepared so that it could be proved that on treatment with alcoholic potash it yields acetic acid and an alcohol melting at 195° .

In these Proc. of June 25, 1905 p. 137 it was stated that the same product has been found by one of us (C.) in the “djelutung” derived from the juice of varieties of *Dyera*. The identity was shown by a comparison of the melting points and by melting point determinations of mixtures of the two substances.

A sufficient quantity was now at disposal to determine the nature of the compound.

In the first place, the substance was recrystallised a few times and finally obtained in beautiful, long, hard needles which melted at 235° (corr. m. p. 240° — 241°).

On analysis (combustion with lead chromate) the following results were obtained:

		Calculated for $C_{22}H_{34}O$,
C	81.96, 82.08.	C 82.06
H	11.24, 11.27.	H 11.11

The compound was found to be dextrorotatory. For the specific rotatory power in a chloroform solution $[\alpha]_D = 81^{\circ}.1$ was found.

As stated above, the substance melting at 235° when boiled with

¹⁾ B. B. 37 (1904) S. 3443.

alcoholic potash yields acetic acid, which was converted into the silver salt. A silver determination gave 64.2 %, theory 64.67 %.

The alcohol formed on saponification was a colorless substance crystallising in long, thin needles and melting at 195° (corr. m. p. 197°—197.5°).

The elementary analysis (with lead chromate) gave:

			Calculated for $C_{10}H_{16}O$.
C	84.27, 84.12, 84.32		84.50
H	11.97, 11.91, 11.99		11.76

This alcohol has also a dextrorotatory power. In a chloroform solution it has $[\alpha]_D = 88^\circ$, and in a benzene solution $[\alpha]_D = 98^\circ$.

On treatment with benzoyl chloride and pyridine, the alcohol readily yields a benzoate which crystallises in beautiful rectangular little plates and melts at 230° (corr. m. p. 234°—235°).

After perusing the literature; it now appeared that the alcohol melting at 195° is identical with β -amyrine which occurs in elemi resin and has been investigated and described with great care by VESTERBERG ¹⁾. Not only do the melting points of the alcohol obtained from Payena Leerii-gutta percha and "djelutung", of the acetate and the benzoate agree perfectly with the melting points determined by VESTERBERG for β -amyrine and its acetate and benzoate, but in addition the values found for the specific rotatory power of the alcohol from "djelutung" and its acetate differ so little from those which he states for β -amyrine and its acetate ²⁾ that the difference may be safely ascribed to experimental errors caused by working with dilute solutions.

β -Amyrine has also been found afterwards by TSCHIRCH ³⁾ in the resin of Protium Carana. It is stated, however, to differ from the common β -amyrine by being optically inactive, which seems somewhat strange. It should be remarked, however, that the cinnamic ester of lupeol described by TSCHIRCH ⁴⁾ about the same period under the name of crystal-albane was also declared to be inactive, although we have found this substance having a decided dextrorotatory power. A further investigation is therefore a desideratum.

MAREK ⁵⁾ has obtained from the milky juice of *Asclepias syriaca* a substance melting at 232°—233°, the melting point of which could be raised by repeated crystallisation to 239°—240°. Its analysis led

¹⁾ B. B. 20 (1887) S. 1242; 23 (1890) S. 3196.

²⁾ VESTERBERG states for β -amyrine (in benzene) $[\alpha]_D = 99^\circ.81$.
for the acetate (in benzene) $[\alpha]_D = 78^\circ.6$.

³⁾ Arch. d. Pharm. 241 S. 149.

⁴⁾ Ibid 241 S. 483.

⁵⁾ Journ. prakt. Chem. Bd. 68 (1903) S. 385 and 449.

to the formula $C_{11}H_{16}O_2$ and on saponification it yielded acetic acid and an alcohol melting at 192° — 193° having the formula $C_{10}H_{16}O$. The benzoate from the alcohol melted at 229° — 230° .

It can hardly be doubted that MAREK has been working with the acetic ester of β -amyrine. Fortunately, he has not given a name to the product isolated by him, and hence, has not unnecessarily increased the already existing confusion.

Undoubtedly, the enormous number of substances said to be obtained from different resins and milky juices will, on closer investigation, be reduced to a more modest number and it will often be shown that pure substances described by different names are one and the same, but could not be identified owing to incomplete description. In other cases, names may have been given wrongly to mixtures or impure substances.

Although it may seem superfluous, it is as well to again point out how necessary it is, when investigating a natural product, to purify the components as completely as possible, to fully describe the properties and particularly to introduce no new names unless one feels certain of really dealing with a new product.

A short time ago, TSCHIRCH¹⁾ communicated the results of an investigation of the components of Balata. From this was isolated a crystallised substance called α -balalbane melting at 231° , the analysis of which led to the formula $C_{17}H_{26}O_2$,

(found C 81.19 H 10.38. calculated C 81.32 H 10.64).

No acids were found by TSCHIRCH on saponification with alcoholic potash as he only looked for crystallised acids²⁾. This made one of us (C.) think that Balata might perhaps also contain acetic esters and that the α -balalbane might be identical with β -amyrine acetate.

It was not difficult to isolate by TSCHIRCH's method the product melting at 231° .

By repeated recrystallisation from acetone, the melting point rose to 235° . On saponification, acetic acid was obtained, also an alcohol melting at 195° . Ester and alcohol mixed, respectively, with β -amyrine acetate and β -amyrine gave no lowering of the melting point, so that α -balalbane is nothing else but β -amyrine acetate; the name α -balalbane may, therefore, be struck out.

University Org. Chem. Lab., *Utrecht*.

¹⁾ Ann. d. Pharm. 243 (1905) S. 358.

²⁾ TSCHIRCH comes to the conclusion that there exist gutta perchas which yield no cinnamic acid on treatment with alcoholic potash, but I have demonstrated this fact previously (B. B. 37 S. 3434), (v. R.).

Mathematics. — "*The quotient of two successive Bessel Functions.*"

By Prof. W. KAPTEYN.

If $I^{v+1}(z)$ and $I^v(z)$ represent two successive Bessel Functions of the first kind, the quotient may be expanded as follows:

$$\frac{I^{v+1}(z)}{I^v(z)} = f_1 z + f_2 z^2 + f_3 z^3 + \dots$$

Of course this equation holds for all values of z within a circle whose radius is equal to the modulus of the first root of the equation $I^v(z) = 0$, zero excepted. EULER and JACOBI have determined the first coefficients of this expansion; we wish to determine the general coefficient.

Starting from the known development

$$\frac{I^{v+1}(z)}{I^v(z)} = \frac{z}{2(v+1)} - \frac{z^3}{2(v+2)} - \frac{z^5}{2(v+3)} - \text{etc.}$$

and putting

$$z^2 = -x \quad 2(v+p) = a_p$$

the question reduces to the determination of the general coefficient in the following equation:

$$\frac{x}{a_1 + \frac{x}{a_2 + \text{etc.}}} = f_1 x - f_2 x^2 + f_3 x^3 - \text{etc.}$$

Let $\frac{P_n}{Q_n}$ stand for the approximating fractions of the continued fraction in the first member, and let

$$\begin{aligned} Q_{2n+1} &= v_0 + v_1 x + v_2 x^2 + \dots + v_n x^n \\ Q_{2n} &= \mu_0 + \mu_1 x + \mu_2 x^2 + \dots + \mu_n x^n \\ Q_{2n-1} &= \lambda_0 + \lambda_1 x + \lambda_2 x^2 + \dots + \lambda_{n-1} x^{n-1} \\ Q_{2n-2} &= \kappa_0 + \kappa_1 x + \kappa_2 x^2 + \dots + \kappa_{n-1} x^{n-1} \\ &\dots \dots \dots \\ Q_{n+2} &= \zeta_0 + \zeta_1 x + \dots + \zeta_r x^r \\ Q_{n+1} &= \varepsilon_0 + \varepsilon_1 x + \dots + \varepsilon_s x^s \end{aligned}$$

where

$$r = \frac{n}{2} + 1 \quad s = \frac{n}{2}$$

when n even, and

$$r = \frac{n+1}{2} \quad s = \frac{n+1}{2}$$

when n is odd, then we find

$$a_1^{n+1} a_2^n a_3^{n-1} \dots a_n^2 a_{n+1} f_{n+1} = (-1)^h \begin{vmatrix} \lambda_1 & \kappa_1 & \iota_1 & \theta_1 \dots \zeta_1 \varepsilon_1 \\ \lambda_2 & \kappa_2 & \iota_2 & \theta_2 \dots \zeta_2 \varepsilon_2 \\ \dots & \dots & \dots & \dots \\ \lambda_{n-2} & \kappa_{n-2} & \iota_{n-2} & \theta_{n-2} \dots 0 \ 0 \\ \lambda_{n-1} & \kappa_{n-1} & 0 & 0 \dots 0 \ 0 \end{vmatrix}$$

In this equation h stands for $\frac{n}{2} - 1$ if n is even and for $\frac{n-1}{2}$ when n is odd. If now we replace a_p by $2(v+p) = 2b_p$ we obtain the following results. Firstly

$$2^{2n+1} b_1^{n+1} b_2^{n-1} \dots b_{\frac{n}{2}+1}^2 b_{\frac{n}{2}+2} \dots b_n^2 b_{n+1} f_{n+1} = (-1)^{\frac{n}{2}-1} \begin{vmatrix} \lambda_1' & \kappa_1' & \iota_1' & \dots \varepsilon_1' \\ \lambda_2' & \kappa_2' & \iota_2' & \dots \varepsilon_2' \\ \dots & \dots & \dots & \dots \\ \lambda_{\frac{n}{2}}' & \kappa_{\frac{n}{2}}' & \iota_{\frac{n}{2}}' & \dots \varepsilon_{\frac{n}{2}}' \\ \lambda_{\frac{n}{2}+1}' & \kappa_{\frac{n}{2}+1}' & \iota_{\frac{n}{2}+1}' & \dots 0 \\ \dots & \dots & \dots & \dots \\ \lambda_{n-2} & \kappa_{n-2} & \iota_{n-2} & \dots 0 \\ \lambda_{n-1} & \kappa_{n-1} & 0 & \dots 0 \end{vmatrix} \dots \dots \dots (I)$$

if n is an even number, and secondly

$$2^{2n+1} b_1^{n+1} b_2^{n+1} \dots b_{\frac{n+1}{2}}^2 b_{\frac{n+3}{2}} \dots b_n^2 b_{n+1} f_{n+1} = (-1)^{\frac{n-1}{2}} \begin{vmatrix} \lambda_1' & \kappa_1' & \iota_1' & \dots \varepsilon_1' \\ \lambda_2' & \kappa_2' & \iota_2' & \dots \varepsilon_2' \\ \dots & \dots & \dots & \dots \\ \lambda_{\frac{n-1}{2}}' & \kappa_{\frac{n-1}{2}}' & \iota_{\frac{n-1}{2}}' & \dots \varepsilon_{\frac{n-1}{2}}' \\ \lambda_{\frac{n+1}{2}} & \kappa_{\frac{n+1}{2}} & \iota_{\frac{n+1}{2}} & \dots \varepsilon_{\frac{n+1}{2}} \\ \dots & \dots & \dots & \dots \\ \lambda_{n-2} & \kappa_{n-2} & \iota_{n-2} & \dots 0 \\ \lambda_{n-1} & \kappa_{n-1} & 0 & \dots 0 \end{vmatrix} \dots \dots \dots (II)$$

if n is an odd number, where

$$\begin{aligned}\lambda'_p &= \frac{(2n-p-1)(2n-p-2)\dots(2n-2p)}{p!} b_{n-p+2}\dots b_{2n-p-1} \\ \kappa'_p &= \frac{(2n-p-2)(2n-p-3)\dots(2n-2p-1)}{p!} b_{n-p+2}\dots b_{2n-p-2} \\ \iota'_p &= \frac{(2n-p-3)(2n-p-4)\dots(2n-2p-2)}{p!} b_{n-p+2}\dots b_{2n-p-3} \\ &\dots\dots\dots \\ \varepsilon'_p &= \frac{(n-p+1)(n-p)\dots(n-2p+2)}{p!} \\ \text{en} \\ \lambda_p &= \frac{(2n-p-1)(2n-p-2)\dots(2n-2p)}{p!} b_{p+1}\dots b_{2n-p-1} \\ \kappa_p &= \frac{(2n-p-2)(2n-p-3)\dots(2n-2p-1)}{p!} b_{p+1}\dots b_{2n-p-2} \\ \iota_p &= \frac{(2n-p-3)(2n-p-4)\dots(2n-2p-2)}{p!} b_{p+1}\dots b_{2n-p-3} \\ &\dots\dots\dots \\ \varepsilon_p &= \frac{(n-p+1)(n-p)\dots(n-2p+2)}{p!} b_{p+1}\dots b_{n-p+1}.\end{aligned}$$

It is of importance to remark that

$\lambda_{n-1} = nb_n$, $\kappa_{n-1} = 1$, $\iota_{n-2} = (n-1)b_{n-1}$, $\theta_{n-2} = 1$ etc.
and that the determinants in the second members of the equations (I) and (II) after the substitution $b_p = v + p$, are respectively polynomials of degrees $\frac{n(n-2)}{4}$ and $\frac{(n-1)^2}{4}$ in v .

Meteorology. - "On frequency curves of barometric heights." By
Dr. J. P. VAN DER STOK.

1. The records of barometric heights, corrected for temperature, observed at Helder three times a day during the years August 1843 to July 1904, have been chosen as an appropriate material for this inquiry into the nature of barometric frequency curves. The number of observations for each month amounts to :

January	5673	July	5673
February	5169	August	5766
March	5646	September	5560
April	5490	October	5766
May	5673	November	5580
June	5490	December	5766
		Total	67252

TABLE I. Frequencies in 10,000 of deviations of barometric heights; positive and negative being taken together.

	Jan.	Febr.	March	Apr.	May	June	July	Aug.	Sept.	Oct.	Nov.	Dec.	Nov. — Febr.	March.—April. Sept.—Oct.	May — Aug.
0 — 0.5 mm.	384	420	417	493	612	705	767	704	539	419	357	377	384	472	697
0.5—1.5	690	837	798	1028	1176	1486	1493	1405	1110	865	726	755	749	950	1390
1.5—2.5	712	779	891	1040	1170	1367	1456	1369	1048	861	750	706	737	943	1340
2.5—3.5	735	752	841	1010	1164	1191	1285	1292	1000	837	737	680	726	922	1233
3.5—4.5	703	799	896	893	1020	1110	1121	1156	950	771	684	692	712	860	1102
4.5—5.5	679	775	702	907	952	933	998	1016	876	775	686	724	716	815	975
5.5—6.5	660	683	751	825	809	804	807	806	783	801	715	660	679	790	806
6.5—7.5	647	615	637	733	767	716	602	651	713	728	655	601	630	703	684
7.5—8.5	636	605	606	633	607	572	428	509	684	638	668	637	637	703	529
8.5—9.5	564	564	579	533	486	402	305	393	550	582	610	553	573	561	306
9.5—10.5	528	493	532	459	391	262	233	280	468	574	557	514	523	508	279
10.5—11.5	498	493	459	362	261	171	179	166	351	452	546	473	485	406	194
11.5—12.5	421	353	406	281	199	105	128	111	283	347	460	445	420	329	136
12.5—13.5	338	342	341	225	126	66	78	73	203	351	395	415	372	199	86
13.5—14.5	267	302	249	166	78	44	42	48	123	257	312	322	301	199	51
14.5—15.5	243	270	235	102	59	32	28	28	88	226	249	307	267	163	37
15.5—16.5	238	238	238	94	60	9	22	12	50	133	195	268	299	128	29
16.5—17.5	225	154	152	59	32	9	13	9	36	118	151	201	183	91	16
17.5—18.5	188	127	84	42	12	3	5	8	35	43	119	147	144	61	8
18.5—19.5	129	116	59	37	10	3	3	4	29	86	118	118	120	48	5
19.5—20.5	94	80	29	23	7	4	5	4	17	30	62	91	88	38	4
20.5—21.5	76	64	29	17	4	3	4	4	8	16	41	70	68	21	2
21.5—22.5	67	56	42	12	3	1	3	10	10	17	29	60	56	21	1
22.5—23.5	69	35	46	8	3	1	5	5	6	16	41	53	46	20	20
23.5—24.5	59	19	18	5	3	1	4	4	4	10	16	28	31	12	12
24.5—25.5	42	23	13	7	2	1	2	4	3	14	16	34	29	9	9
25.5—26.5	29	18	11	2	2	1	2	4	3	2	10	20	19	5	5
26.5—27.5	27	14	6	2	1	1	2	2	2	9	14	24	21	4	4
27.5—28.5	17	14	11	1	1	1	2	2	2	2	17	13	15	3	3
28.5—29.5	8	11	6	1	1	1	2	2	2	2	10	10	10	3	3
29.5—30.5	7	11	3	1	1	1	2	2	2	2	6	12	9	3	3
30.5—31.5	10	7	3	1	1	1	2	2	2	2	2	3	6	1	1
31.5—32.5	6	7	4	1	1	1	2	2	2	2	2	3	5	1	1
32.5—33.5	4	3	4	1	1	1	2	2	2	2	2	2	3	1	1
33.5—34.5	4	1	1	1	1	1	2	2	2	2	2	2	1	1	1
34.5—35.5	1	0	1	1	1	1	2	2	2	2	2	2	1	1	1
35.5—36.5	3	0	0	0	0	0	1	1	1	1	1	0	2	1	1
36.5—37.5	3	0	0	0	0	0	1	1	1	1	1	0	0	0	0
37.5—38.5	1	0	0	0	0	0	1	1	1	1	1	0	0	0	0
38.5—39.5	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1

TABLE II. Differences, W--B, between observed frequencies and frequ. calculated according to exponential law; in 10,000 for every month, in 40,000 for the seasons.

	Jan.	Febr.	March	Apr.	May	June	July	Aug.	Sept.	Oct.	Nov.	Dec.	Sums.		
													Nov. — Febr.	Mrch.—Apr. Sept.—Oct.	May — Aug.
0—0.5	3	3	23	59	30	27	11	40	16	57	60	18	78	155	86
0.5—1.5	94	7	13	56	82	24	10	45	17	86	116	30	233	172	93
1.5—2.5	52	49	48	13	50	12	48	20	56	60	66	69	236	177	34
2.5—3.5	11	42	2	5	20	75	4	19	38	62	68	75	196	97	32
3.5—4.5	18	35	19	47	17	12	15	37	16	74	79	78	140	118	7
4.5—5.5	12	47	60	37	21	36	29	50	14	27	51	25	9	64	64
5.5—6.5	4	10	47	46	7	9	15	13	3	68	32	1	25	158	44
6.5—7.5	30	22	20	43	83	79	28	13	17	52	10	19	1	92	147
7.5—8.5	70	18	7	28	44	80	51	16	94	38	83	60	231	167	79
8.5—9.5	33	30	40	33	37	35	43	29	54	50	70	23	156	168	58
9.5—10.5	84	5	53	24	37	6	20	35	56	104	78	30	197	246	24
10.5—11.5	59	2	39	12	7	14	3	16	23	48	113	37	211	122	34
11.5—12.5	28	30	42	1	3	15	16	13	20	64	85	51	134	68	19
12.5—13.5	12	9	33	2	19	10	7	9	3	23	63	71	131	102	36
13.5—14.5	40	19	15	6	30	10	6	2	30	23	31	21	31	28	44
14.5—15.5	25	28	15	31	11	1	0	5	25	33	6	45	54	8	15
15.5—16.5	7	9	56	7	14	4	6	6	32	19	7	44	53	2	18
16.5—17.5	31	18	4	13	7	3	5	1	22	3	19	10	4	34	0
17.5—18.5	20	13	17	11	1	2	3	3	10	28	24	14	31	66	3
18.5—19.5	12	2	10	3	7	0	2	4	2	30	5	16	21	35	0
19.5—20.5	23	12	15	1	3	0	1	3	1	2	5	20	50	21	2
20.5—21.5	20	11	29	4	0	2	2	3	5	12	11	21	63	47	3
21.5—22.5	11	2	0	1	3	0	1	3	3	13	16	14	43	9	1
22.5—23.5	5	10	18	1	1	0	0	1	5	6	16	5	26	23	3
23.5—24.5	9	16	8	4	4	0	4	4	4	5	18	19	8	13	6
24.5—25.5	0	3	5	0	0	3	3	3	1	7	11	9	5	10	1
25.5—26.5	2	4	3	4	0	4	4	4	7	4	9	1	6	3	3
26.5—27.5	7	2	4	1	1	2	1	4	4	1	2	3	16	1	4
27.5—28.5	2	2	4	0	0	0	0	1	1	1	7	3	10	4	3
28.5—29.5	7	4	1	3	3	1	3	1	3	1	2	3	8	3	1

TABLE III. Skew-differences, $P-N$, of positive and negative deviations.

	Jan.	Febr.	March	Apr.	May	June	July	Aug.	Sept.	Oct.	Nov.	Dec.	Sums.		
													Nov. Febr.	March— Sept.—Oct.	May — Aug.
0.5—1.5	6	21	30	0	16	80	43	1	46	23	12	15	54	7	140
1.5—2.5	10	3	55	106	48	139	114	77	48	71	22	62	91	280	318
2.5—3.5	25	56	81	122	54	115	79	164	68	37	69	60	210	308	412
3.5—4.5	93	75	16	135	44	114	75	92	90	61	50	20	238	302	325
4.5—5.5	95	89	42	147	61	79	136	50	86	57	86	60	330	332	345
5.5—6.5	118	105	79	121	80	78	133	126	85	83	91	86	400	368	398
6.5—7.5	133	127	111	151	37	48	74	97	95	138	51	45	356	395	256
7.5—8.5	102	83	16	113	43	2	44	44	139	94	60	89	334	411	426
8.5—9.5	128	108	13	29	26	20	5	19	144	62	104	97	437	242	30
9.5—10.5	74	77	80	15	19	10	31	28	38	40	109	108	368	173	50
10.5—11.5	72	33	75	56	19	15	48	42	19	60	154	75	334	98	39
11.5—12.5	77	25	24	45	17	42	31	45	3	7	112	47	261	15	121
12.5—13.5	50	32	17	25	6	11	46	33	9	3	93	57	232	40	115
13.5—14.5	33	12	25	14	19	35	30	32	43	35	20	38	103	3	89
14.5—15.5	44	34	25	16	13	20	26	18	62	57	81	36	81	57	100
15.5—16.5	44	21	24	33	30	7	13	12	34	57	37	27	107	119	92
16.5—17.5	5	2	2	23	12	3	7	9	31	43	20	30	126	108	30
17.5—18.5	26	25	19	26	10	3	5	4	17	38	38	47	142	64	4
18.5—19.5	25	20	22	29	7	3	3	4	29	23	26	38	148	47	—
19.5—20.5	40	14	39	19	4	—	—	5	10	16	25	31	148	47	—
20.5—21.5	32	26	23	17	—	—	—	4	8	17	31	47	148	47	—
21.5—22.5	41	32	18	8	—	—	—	—	6	10	16	38	148	47	—
22.5—23.5	39	19	16	5	—	—	—	—	4	10	16	38	148	47	—
23.5—24.5	47	29	16	8	—	—	—	—	3	14	16	30	107	37	—
24.5—25.5	38	23	13	7	—	—	—	—	3	2	10	20	75	19	—
25.5—26.5	27	18	11	2	—	—	—	—	4	2	14	21	86	20	—
26.5—27.5	29	22	6	2	—	—	—	—	3	2	17	13	61	16	—
27.5—28.5	17	14	11	1	—	—	—	—	2	2	10	12	39	14	—
28.5—29.5	8	11	6	4	—	—	—	—	2	—	6	12	36	11	—
29.5—30.5	7	11	9	—	—	—	—	—	2	—	2	3	26	3	—
30.5—31.5	10	7	3	—	—	—	—	—	2	—	2	5	20	4	—
31.5—32.5	6	4	—	—	—	—	—	—	—	—	—	3	12	—	—
32.5—33.5	4	1	—	—	—	—	—	—	—	—	—	2	4	—	—
33.5—34.5	1	0	—	—	—	—	—	—	—	—	—	2	3	—	—
34.5—35.5	1	0	—	—	—	—	—	—	—	—	—	3	7	—	—
35.5—36.5	4	0	—	—	—	—	—	—	—	—	—	0	3	—	—
36.5—37.5	3	0	—	—	—	—	—	—	—	—	—	0	1	—	—
37.5—38.5	1	1	—	—	—	—	—	—	—	—	—	5	7	—	—
38.5 enl.	1	1	—	—	—	—	—	—	—	—	—	—	1	—	—

In registering the observations the decimals have been omitted, so that the number of occurrences corresponding with a height of P mm. includes all values between $P + 0.5$ and $P - 0.5$ mm.

Owing to this simplification the amount of labour is less than would appear from the great number of data. The next work to do was to multiply the frequency numbers with a factor such that the total number for each month amounted to 10.000. The frequencies thus obtained correspond with expressions for the probability of occurrence expressed in 10.000th parts of unity. Then the average height was calculated and, by means of simple, linear interpolation the whole curve shifted in such a manner that the new frequencies correspond with deviations from the average value expressed in multiples of whole numbers. This has been done not only with a view of abridging the computations of the moments of the second and third order but principally in order to obtain an evaluation of the skewness of the curves, which may be defined as the inequality of frequency for equal positive and negative deviations from the arithmetical mean. If of such a series of data the frequencies corresponding with equal deviations are taken together, no account being taken of their sign, the skewness is eliminated, and the numbers obtained in this way may be considered as belonging to a symmetrical curve (Table I).

For this curve we calculate the factor of precision (stability) and investigate in how far the actual curve agrees or disagrees with the curve of the normal exponential law (Table II).

As has been mentioned above, the inequalities of frequencies for equal deviations of opposite sign have been taken as a measure of the skewness.

Tables I—III show, separately for each month, the sums and differences thus formed. The numbers of Table I added to those of Table III will give twice the number of frequencies corresponding to positive deviations, their differences being twice that corresponding to negative deviations. The values given for Winter, Summer and Spring-Autumn are obtained by taking together the corresponding numbers in the same Tables; consequently they are not quite identical with the numbers which would have been obtained if the frequencies for these seasons had been calculated from the absolute heights, instead of, as has been done here, from the deviations; in the latter the annual variation has been left out of consideration. The annual variation, however, being very small, this will not influence the results to an appreciable degree.

2. Table IV shows the results of the treatment of the frequencies given in Table I, as indicated. If the deviation from the arithmetical mean is denoted by ε , then :

$$M = \sqrt{\frac{|\varepsilon^2|}{n-1}}, \quad \vartheta = \frac{|\varepsilon|}{n}, \quad h = \frac{1}{M\sqrt{2}}, \quad h' = \frac{1}{\vartheta\sqrt{\pi}}, \quad \pi = \frac{2M^2}{\vartheta^2}.$$

TABLE IV.

	M	ϑ	h	h'	π
Jan.	10.261 mM.	8.272 mM.	0.0689	0.0682	3.081
Febr.	9.522	7.597	0.0743	0.0743	3.141
Mrch.	8.969	7.194	0.0788	0.0784	3.109
Apr.	7.280	5.864	0.0971	0.0962	3.083
May	6.218	5.022	0.1136	0.1124	3.067
June	5.391	4.322	0.1312	0.1305	3.112
July	5.276	4.169	0.1340	0.1354	3.204
Aug.	5.374	4.300	0.1316	0.1312	3.125
Sept.	6.972	5.602	0.1014	0.1007	3.098
Oct.	8.372	6.832	0.0845	0.0826	3.003
Nov.	9.490	9.006	0.0745	0.0725	2.974
Dec.	10.085	8.173	0.0701	0.0690	3.045

From this summary it appears that the frequency curve of barometric heights, as derived from observations made at Helder, shows systematic departures from the normal curve corresponding to the exponential law. For all months (except February and July) h is greater than h' ; in February these factors are equal and the curve is nearly a normal one, in July $h' > h$.

In agreement with this result the calculated value of π is always (except in the two months mentioned) less than its true value; the departures from the normal law are greatest in winter, smallest in summer time.

It may be noticed that the departures from the normal curve, given in table II, are generally of an opposite sign to those which are found in the great majority of series of errors: whereas for the latter the rule holds that small deviations occur oftener than is required by the normal law (in which case $h' > h$ and $\pi \text{ calc.} > \pi$),

here the reverse obtains, the frequency of barometric heights showing a deficit for small and a surplus for moderate deviations.

In an earlier paper (this volume p. 314) I have shown that, in taking together series with different factors of steadiness, each series occurring with equal subfrequency, we must expect to find too great a number of small deviations.

From this follows the apparently somewhat paradoxical conclusion, that a sum of frequency numbers as those of barometric deviations, all showing negative differences for small deviations, may, when taken together, lead to a resulting curve in which these differences have vanished or even turned positive.

This conclusion is of some importance because an investigation into the frequency of barometric heights, in which the different months are not treated separately, may lead to normal curves (the skewness being left out of account) whereas in fact no normal curve exists and appears only as an artificial consequence of the combination of incomparable frequency numbers.

The exceptional behaviour of the months of February and July might then be explained by assuming that the different series of barometric curves corresponding with different winds (barometric windrose) are more differentiated in these two months than in the other ones.

A second remark is that frequency numbers as given in Table I cannot be accepted as a measure for the variability of the atmospheric pressure in the course of a month, at least not if we adhere to the conception of this variability as generally admitted.

On the one hand we have here to do with the superposition of two kinds of variability, 1st the secular variability as shown by the variability from year to year of monthly means and 2nd the variability from day to day, which might be called the interior variability for the month in question ; it is the latter definition which corresponds with the usual conception.

On the other hand, daily means or observations taken at fixed hours are by no means to be regarded as being independent of each other.

The questions, therefore, arise : how can we separate the two kinds of variability, and to what degree are daily mean values of barometric observations to be taken as dependent upon each other in the different months.

For a knowledge of the climate of a place the latter question is of importance ; it might also be formulated thus : what is the average duration of a barometric disturbance, a question which can hardly be answered by means of direct investigation.

TABLE V.

	Observ. <i>W.</i>	Exp. L. <i>B.</i>	<i>W-B</i>		Observ. <i>W.</i>	Exp. L. <i>B.</i>	<i>W-B</i>
0—0.5	515	496	+ 19	14.5—15.5	118	172	— 24
0.5—1.5	1025	996	+ 29	15.5—16.5	125	134	— 9
1.5—2.5	1001	962	+ 39	16.5—17.5	100	104	— 4
2.5—3.5	956	935	+ 21	17.5—18.5	75	79	— 4
3.5—4.5	888	875	+ 13	18.5—19.5	58	59	— 1
4.5—5.5	846	826	+ 20	19.5—20.5	43	45	— 2
5.5—6.5	756	757	— 1	20.5—21.5	33	29	+ 4
6.5—7.5	674	676	— 2	21.5—22.5	25	23	+ 2
7.5—8.5	591	608	— 17	22.5—23.5	21	16	+ 5
8.5—9.5	519	526	— 7	23.5—24.5	13	12	+ 1
9.5—10.5	437	459	— 22	24.5—25.5	13	7	+ 6
10.5—11.5	363	384	— 21	25.5—26.5	10	5	+ 5
11.5—12.5	304	322	— 18	26.5—27.5	7	3	+ 4
12.5—13.5	244	268	— 24	27.5—28.5	6	2	+ 4
13.5—14.5	191	216	— 25	28.5—etc.	13	4	+ 9

The first problem is identical with the calculation of the probability of an event $a + b$, when a and b follow the normal law and are independent of each other.

This problem of the superposition of two laws of errors has been already treated by BESSEL ¹⁾ and subsequently d'OCAGNE ²⁾ gave a general solution for the superposition of several groups of errors.

It appears that, if H be the factor of stability of the secular and h_1 that of the interior variability, the resulting deviations also follow the normal law, the new factor h being determined by:

$$h = \frac{H h_1}{\sqrt{H^2 + h_1^2}}.$$

From the values of h given in Table IV and those of H calculated from monthly means we can, therefore, deduce that of h_1 :

¹⁾ Untersuchungen über die Wahrscheinlichkeit der Beobachtungsfehler. Astr. Nachr. XV, 1838.

²⁾ Sur la composition des lois d'erreurs de situation d'un point. C. R. Acad. sc. CXVIII, 1894.

TABLE VI.

	H	h	h_1	D
Jan.	0.1411	0.0689	0.0787	7.52
Febr.	0.1458	0.0743	0.0864	7.46
March	0.1682	0.0788	0.0852	6.82
Apr.	0.2105	0.0971	0.1094	6.49
May	0.3019	0.1136	0.1226	4.46
June	0.3181	0.1312	0.1440	5.19
July	0.3392	0.1340	0.1459	4.92
Aug.	0.3330	0.1316	0.1432	5.00
Sept.	0.2350	0.1014	0.1123	5.74
Oct.	0.2113	0.1845	0.0926	5.12
Nov.	0.1892	0.0745	0.0810	4.81
Dec.	0.1419	0.0701	0.0806	7.82

the final aim in inquiries of this kind to come to a rational expression for the frequency of barometric deviations as a function of the distance of centres of depressions and of their average depth and extent but, even if we assume the most simple relations between pressure and distance of the centrum, we must expect to find rather complicated, exponential expressions, which can be treated only by expansion into series. It is, therefore, desirable to summarize the characteristics of the frequency curve in an empirical formula of the form:

$$e^{-H^2x^2} (A + Bx + Cx^2 + Dx^3 + Ex^4). \quad (3)$$

The constants of this formula can be easily determined and, if we succeed in establishing a rational expression, there will probably be no difficulty in indicating their meteorological meaning.

The frequency curve, positive and negative deviations being taken together (Table I), is then represented by the expression:

$$Z = 2e^{-H^2x^2} (A + Cx^2 + Ex^4), \quad (4)$$

which represents a symmetrical curve, and the formula for the differences of Table III becomes:

$$Y = 2e^{-H^2x^2} (Bx + Dx^3). \quad (5)$$

If, as in our case, the deviations x are departures from the arithmetical mean,

$$\int_0^\infty Z dx = 1, \quad \int_0^\infty Zx dx = \mu_1 = \vartheta, \quad \int_0^\infty Zx^2 dx = \mu_2 = M^2$$

$$\int_0^\infty Zx^3 dx = \mu_3 \text{ etc.}; \quad \int_0^\infty Yx dx = 0. \quad \dots \quad (6)$$

For the determination of the constants of form. (4) we then have the four relations:

$$\left. \begin{aligned} A + \frac{C}{2H^2} + \frac{1.3 E}{4H^4} &= \frac{H}{\sqrt{\pi}} \\ A + \frac{2C}{2H^2} + \frac{2.4 E}{4H^4} &= H^2 \mu_1 \\ A + \frac{3C}{2H^2} + \frac{3.5 E}{4H^4} &= \frac{2H^2 \mu_2}{\sqrt{\pi}} \\ A + \frac{4C}{2H^2} + \frac{4.6 E}{4H^4} &= H^4 \mu_3 \end{aligned} \right\} \dots \dots (7)$$

Multiplying resp. by 1, — 3, + 3 and — 1 and adding, we find:

$$H^2 - a H^2 + b H - c = 0$$

$$a = \frac{6\mu_2}{\mu_3 \sqrt{\pi}}, \quad b = \frac{3\mu_1}{\mu_3}, \quad c = \frac{1}{\mu_3 \sqrt{\pi}},$$

or, because:

$$\mu_1 = \frac{1}{h' \sqrt{\pi}}, \quad \mu_2 = \frac{1}{2h^2}, \quad \mu_3 = \frac{1}{h''^2 \sqrt{\pi}},$$

$$\frac{H^2}{h''^2} - \frac{3H^2}{h^2} + \frac{3H}{h'} - 1 = 0 \quad \dots \dots (8)$$

From this equation possible values for H can be derived, but not in an advantageous manner as the quantities h , h' and h'' generally are only slightly different.

In practice, i. e. if we come to expression (4) by expansion of a theoretical formula, the problem will probably be less difficult, as the constants H and A or H and h will not be independent of each other, and it will be possible to reduce the four equations (7) to three or two.

In this preliminary investigation we confine ourselves to the most simple case that $H = h$ which, as it will appear, leads to satisfactory results.

Putting

$$\frac{h-h'}{h'} = K,$$

we find:

$$A \vee \pi = h(1 - 3 \cdot K)$$

$$C \vee \pi = 12 \, h^3 \, K$$

$$E \vee \pi = -4h^5 K \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

The position of the points of intersection of the observed frequency curve with that calculated by assuming the simple exponential law to hold good (the points where in Table II the numbers change their sign) is determined by the equation :

$$(A + Ca^2 + Ea^4) \sqrt{\pi} - h = 0,$$

Or :

$$\alpha^4 - \frac{3}{h^2} \alpha^3 + \frac{3}{4h^4} = 0. \quad (10)$$

$$\alpha_1 = \frac{0.525}{h}, \quad \alpha_2 = \frac{1.651}{h}.$$

In fact Table II shows that there are no more than two well defined points of intersection, which justifies the omission of higher powers than the fourth in form. (4).

Tabel VII shows the values of the constants of (4) and the values of α calculated with the help of form. (9) and (10).

It is evident that, if form. (4) and the values of its constants determined in the way indicated give a good representation of the observed facts, the values of the coefficient A must be nearly equal

TABLE VII.

	<i>A</i>		<i>C</i>	<i>E</i>	<i>z</i> ₁	<i>z</i> ₂
	Calculated.	Observed.				
Jan.	377×10^{-4}	381×10^{-4}	227×10^{-7}	— 36×10^{-9}	7.62	23.96
Febr.	419	420	0	0	7.07	22.22
March	438	417	142	— 35	6.66	20.95
Apr.	532	493	310	— 182	5.41	17.00
May	620	612	662	— 456	4.62	14.53
June	728	705	532	— 471	4.00	12.58
July	779	767	— 1581	+ 1008	3.92	12.32
Aug.	734	704	588	— 340	3.99	12.55
Sept.	560	559	491	— 168	5.18	16.28
Oct.	444	419	910	— 224	6.21	19.54
Nov.	386	357	772	— 143	7.05	22.16
Dec.	377	377	372	— 61	7.49	23.55

to the frequencies corresponding with the deviations 0—0.5 mm., as given in Table I, so that the greater or less degree of agreement between these values may be taken as a criterion for the proposed assumption $H = h$.

In order to show that this agreement is fairly satisfactory, the observed frequencies between the limits 0 and 0.5 are given once more besides the calculated values of A .

If we compare the situation of the intersection points as shown in Table II and as calculated according to form. (10), we see that the situation of the first point of intersection agrees well with the observed facts, but that the second points α_2 , as calculated, correspond with greater deviations than occur in reality.

As this second point of intersection naturally coincides with small frequencies the degree of precision of which is questionable, it seems difficult to decide whether these differences may be ascribed to insufficiency of material, to the omission of a possible fourth term in form. (4), or to an error introduced by the supposition $H = h$; as the calculated values of α_2 are jointly too great, the latter cause has to be regarded as the most probable one.

4. The fact that in Table III, in which a measure is given for the skewness of the curves, except for $\varepsilon = 0$, only one zero-value occurs, proves that in form. (5) the addition of a third term is certainly not required. The calculation of the constants B and D as well as the determination of the point of intersection β can, therefore, easily be made.

As :

$$\int_0^{\infty} Yx dx = 0$$

we find immediately :

$$B + \frac{3}{2} \frac{D}{h^2} = 0, \dots \dots \dots (11)$$

whereas :

$$\int_0^{\infty} Y dx = \frac{B}{h^2} + \frac{D}{h^4} = v = p - n. \dots \dots \dots (12)$$

denotes the surplus of positive over negative deviations.

If we take the absolute sum of positive and negative deviations as a measure for the skewness s :

$$s = p + n = 2 \int_0^{\beta} Y dx - \int_0^{\infty} Y dx = 2 \int_0^{\beta} Y dx - v,$$

or :

$$s + v = 2 \int_0^{\beta} Y dx \dots \dots \dots (13)$$

The situation of the point of intersection β is determined by the equation :

$$B + D\beta^2 = 0 \dots \dots \dots (14)$$

By (11) and (12) :

$$B = 3 h^2 v, D = -2 h^4 v \dots \dots \dots (15)$$

$$\beta^2 h^2 = \frac{3}{2} \dots \dots \dots (16)$$

With the help of (13) we find from these values :

$$s = v (1 + 4e^{-3/2}),$$

$$\frac{s}{v} = \frac{p + n}{p - n} = 1.89, \quad \frac{p}{n} = 3.25 \dots \dots \dots (17)$$

By means of the values v or s , to be taken from Table III, the constants of form (5) as well as the position of the point of intersection can, therefore, be determined ; we choose v , so that a comparison of the calculated and observed values of s/v or p/n may serve as a criterion for the method followed in calculating the constants of the empirical formula.

TABLE VIII.

	Observed.		Calculated.		
	v	s	B	D	β
Jan.	707×10^{-4}	1505×10^{-4}	101×10^{-5}	32×10^{-7}	17.8
Febr.	606	1184	100	37	16.5
March	467	923	87	36	15.5
Apr.	639	1277	181	114	12.6
May	423	576	163	141	10.5
June	483	668	249	286	9.3
July	486	998	262	313	9.1
Aug.	426	908	295	256	9.3
Sept.	463	1073	143	98	12.1
Oct.	429	748	92	44	14.5
Nov.	599	1467	100	37	16.4
Dec.	605	1309	89	29	17.5
Mean	528	1053			

The average values of v and s show a satisfactory agreement with the form. (17):

$$\frac{s}{v} = \frac{1053}{528} = 1.99$$

From the aggregate values given in Table III for three seasons we find:

	Sums.				
	p	n	$p + n = s$	s	p/n
Winter	3849	1340	5189	12.97 %	2.87
Spring-Autumn	2959	937	3896	9.74	3.16
Summer	2380	747	3127	7.82	3.19

For the values of β in these three seasons:

	Observ. Tab. III	Calc. Tab. VII
Winter	17	17.05
Spring-Autumn	14	13.68
Summer	9.5	9.55

Anatomy. — "*Anatomical research about cerebellar connections.*"

By L. J. J. MUSKENS. (second communication). (Communicated by Prof. C. WINKLER).

A comparative examination into different species of mammals I have thought desirable in order to get information about the course of the axis-cylinders arising from the cortex cerebelli. The development of our knowledge in this matter in the last 15 years has resulted in that at the present time the following question has been placed in the center of discussion: do the strands of fibres, which form the superior Crus cerebelli, arise from the cortex cerebelli strictiore sensu or have we to regard the basal cerebellar nuclei as an indispensable intermediary for all these cortico-fugal nervefibres? On the one hand we find in some rodentia in the lobus petrosus cerebelli exclusively cortex and white matter (squirrel), on the other hand we find in others (rabbit) equally a part of the nucleus dentatus situated in the peduncle of that lobe. In both animals the lobus petrosus is situated in a separate bony hole. We find in this lobe therefore a very fortunate opportunity for operative procedure therein, leaving the other neighbouring central structures and also the semi-circular canals intact. We can here in a comparative physiological way find an answer on the above question and at the same time avoid a large cranial aperture.

Since MARCHI stated, that after large lesions as hemi-exstirpation of the cerebellum a number of nerve-strands degenerate up to the mesencephalon and down to the spinal cord, it is notable, that subsequently MAHAIM, FERRIER and TURNER, R. RUSSELL, THOMAS and especially PROBST and VAN GEHUCHTEN have more and more directed their attention to smaller and smaller lesions, so that it became more and more clear, that most of the degenerations, found by MARCHI, were caused by affection of neighbouring parts. Finally have CLARKE and HORSLEY recently succeeded in stating definitely, that all fibres of the superior crus cerebelli do not arise from the cortex, but from the basal nuclei. Their material was larger than that of any of the precedent investigators and only very limited exstirpations, mostly without any lesion of the nuclei, were used. If the lesion was limited and the cerebellar cortex exclusively hurt, never the degeneration was found further than the nuclei. They stated moreover, which parts of the cortex are directly connected with special parts of the basal nuclei.

Independently of this result the examination of my own material (experiments on the lobus petrosus in different rodentia) tends clearly to reinforce their conclusion. Whereas in the case of the squirrel (where only cortical and white matter in the lobus petrosus cerebelli -- inexactly called flocculus -- can be hurt) the degeneration stops short in the lateral part of the dentate nucleus, we find in the rabbit always a part -- especially and exclusively the middle third part of the superior crus cerebelli on cross section -- degenerated. These degenerated fibres could be followed in the series of sections up to the lesion. Here, in the case of the rabbit, we had removed a number of ganglioncells, situated in the peduncle of the lobus petrosus and being contiguous to the nucleus dentatus.

We see therefore that as well the MARCHI-work in the same species as experiments in kin animal groups lead to the same answer to our question viz. that only the ganglioncells of the basal nuclei and not the cells of PURKINJÉ, have to be regarded as the origin of the degenerations after the cerebellar lesion. The last reserve left in this matter by EDINGER can therefore, so it appears to me, be abandoned.

In accordance with the above investigators and also with my former communication in These Proc. VII p. 202 about experiments in rabbits I could not find in the spinal cord of the squirrels, examined, any dégénération. Regarding the middle cerebellar peduncle, the relations are more complicated and need further research.

Chemistry. — "*On the simplest hydrocarbon with two conjugated systems of double bonds, 1.3.5. hexatriene.*" By Prof. P. VAN ROMBURGH and W. VAN DORSSEN.

In 1878 TILDEN¹⁾ advanced the hypothesis that the terpenes might be derivatives of a hydrocarbon of the formula :



At the meeting of the Assoc. franç. pour l'avanc. des Sciences in Paris 28 Aug. 1878, FRANCHIMONT pronounced the same opinion and suggested that this compound might, perhaps, be obtained by eliminating of the two chlorine atoms from acrolein chloride. The efforts made by one of us (v. R.) many years ago to prepare that hydrocarbon in this manner did not prove successful. The researches on terpenes which afterwards definitely led to the result that, in the case of these substances, we are dealing with cyclic compounds made the above cited hydrocarbon recede into the background.

The views of THIELE on conjugated systems of double bonds, and the researches originated therefrom, in addition to the studies on the aliphatic terpenes myrcene and ocimene, hydrocarbons in which the existence of three double-bonds has been proved by different investigators, have again drawn our attention to the 1.3.5 hexatriene, because it would represent the simplest hydrocarbon in which occur three double linkings that also form two conjugated systems.

One of us (v. R.) has pointed out previously that one of the methods which might lead to the desired product consists in the action of metals on 3.4 dichloro-1.5 hexadiene.

The investigations of GRINER²⁾ have acquainted us with the analogous bromine compound which is formed by the action of phosphorus tribromide on s. divinyl glycol. We have treated this substance, prepared according to GRINER's directions, with metals but have not yet succeeded in preparing the hydrocarbon in that way. There was however, another way still at our disposal to gain our object, namely, by starting from s. divinyl glycol and converting this into a formic ester.

It is known that the formates of polyhydric alcohols, in which occur a OH-group and a formic acid-residue connected with two C-atoms linked together, yield, on heating, unsaturated compounds with elimination of carbon dioxide and water. It was now obvious to prepare the monoformate of divinyl glycol. We endeavoured to do this by heating this glycol with oxalic acid but obtained, mainly, brownish

¹⁾ Journ. chem. Soc. 1878. p. 80.

²⁾ Ann. d. Chim. et d. Phys. [6] 26 (1892) p. 305.

compounds not looking fit for further investigation. By cautious treatment with formic acid the diformate was, however, readily obtained (see p. 544).

In order to convert this into the hydrocarbon, a reaction was applied which one of us had previously used for preparing allyl alcohol from the diformate of glycerol, and which consists in heating that compound with glycerol.

And, indeed, a mixture of the diformate of divinyl glycol with the glycol when heated slowly, first at 165° and then gradually to 200° , evolves carbon dioxide and a little carbon monoxide and yields a distillate consisting of two layers, the upper one of which consists of a hydrocarbon.

The triformate of glycerol, like the diformate of divinyl glycol, may be distilled without notable decomposition by heating it somewhat rapidly at the ordinary pressure. Recently one of us (v. R.) found however that it is decomposed by prolonged heating at a temperature a little below the boiling point and it then yields the same decomposition products as the diformate of glycerol.

If now the diformate of s. divinyl glycol is heated at 165° and the temperature allowed to rise very slowly, an evolution of gas is observed and in the receiver is collected a liquid consisting of two layers. The upper layer again consists of a hydrocarbon identical with the one cited above.

Probably, the simplest way to explain this reaction is to assume that the diformate contains a little monoformate which is decomposed in the desired sense, with formation of water which in turn regenerates monoformate from the diformate. Finally, a residue consisting of glycol (respectively, polyglycols) is obtained and in the distillate a little formic acid is found, besides water, whilst the gases evolved consist of carbon dioxide and carbon monoxide. The last method appears to give a better yield than the first one.

The hydrocarbon formed is separated and distilled, the portion distilling up to 95° being collected. It is then dried over a piece of caustic potash, which also removes traces of formic acid and then rectified a few times over metallic sodium.

It then forms a colourless, strongly refractive liquid with a slight pungent odour; in contact with the air it appears to slowly oxidise. The boiling point lies between 77° — 82° , the main fraction boils between $78^{\circ},5$ — 80° (corr.; pressure 766 m.m.)

The analysis and the vapour density gave values leading to the composition C_6H_8 .

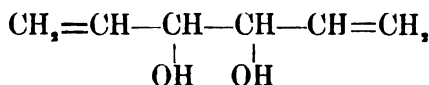
For the physical constants of the main fraction was found :

Spec. gr.₁₀ 0,7565 $n_{D_{10}}$ 1.49856.

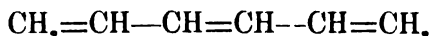
If we calculate the molecular refraction from these data, with the aid of the formula of LORENTZ—LORENZ, we find $MR = 31,03$, whilst for C_6H_8 is found $MR = 28,53$ assuming that the hydrocarbon possesses three double bonds, and making use of the atomic refractions of CONRADY¹⁾ and the increment for the double bond.

The difference of 2,5 between the calculated and found molecular refraction is a striking one. According to BRÜHL²⁾ excesses always occur with substances with a conjugated system of double bonds. In the aliphatic terpene ocimene, an excess (to the extent of 1.76) is also found, and this assumes an extraordinarily large proportion in the case of allo-ocimene.³⁾

As regards the structural formula of the hydrocarbon obtained, its formation from

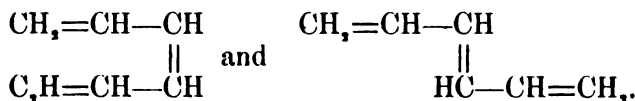


by the elimination of the two OH-groups by means of formic acid points to the formula:

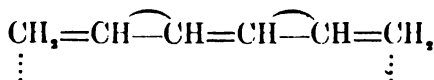


which indeed represents 1.3.5-hexatriene.

A glance at this formula shows that it may appear in two geometrical isomeric forms, namely in the *cis* and *trans* form⁴⁾:



If, with THIELE⁵⁾, we accept partial valencies the formula of 1.3.5-hexatriene should be written:



Unsaturated hydrocarbons with a conjugated system readily take

¹⁾ Zeitschr. physik. Chem. **3**, 226.

²⁾ B.B. **38**, 768.

³⁾ C. J. ENKLAAR, Dissertation 1905. Compare literature on the subject p. 87.

⁴⁾ Probably, the hydrocarbon is a mixture of both. In the fractionation, besides the main fraction, a distillate could be obtained boiling between 77.5° and 78° 5 (sp. gr.₁₀ 0.7558, $n_{D_{10}}$ 1.494 MR 30.8), also a final fraction boiling between 80°—82° (sp. gr.₁₀ 0.7584, $n_{D_{10}}$ 1.503, MR 31.2). We hope to repeat the experiment on a larger scale.

⁵⁾ Ann. **306**. 94.

up hydrogen on treatment with absolute alcohol and metallic sodium. In the reduction of our own hydrocarbon, 2,4 hexadiene might be expected in the first place, although, a priori the formation of other hexadienes is not to be excluded. In the 2,4 hexadiene



we have again, however a compound with a conjugated system which might be further hydrogenated to hexene 3.

In fact, our hydrocarbon when treated with boiling absolute alcohol and metallic sodium takes up hydrogen. The study of the product (or products) of the reaction is not facilitated by the contradictory statements found in the literature about the hexadienes. A future communication will treat more extensively of this reaction and also of the original hydrocarbon whose structure we will try to determine also by other methods. We may state further that a dibromine addition compound has been prepared melting at 89—90° and a tetra-compound melting at 115°.

University. Org. Chem. Lab. *Utrecht*.

Chemistry. — “*On the hidden equilibria in the p, x -sections below the eutectic point*”. By DR. A. SMITS. (Communicated by Prof. H. W. BAKHUIS ROOZEBOOM).

The p, x -sections of binary systems in the neighbourhood of the eutectic point have been fully discussed by BAKHUIS ROOZEBOOM¹⁾; in this the course of the solubility isotherms in the unstable and metastable region were, however, not examined. This problem could only be taken in hand after VAN DER WAALS' paper²⁾ on: “*The equilibrium between a solid body and a fluid phase, especially in the neighbourhood of the critical state*” had been published.

Availing myself of this paper I shall discuss the just-mentioned problem, and show briefly in what way the stable region is connected with the metastable and unstable region.

If for the two substances A and B the volume in solid state is larger than in liquid state, these substances will have negative melting-point curves, i. e. $\frac{dp}{dt}$ will be negative, and the melting-point curve will therefore pass to lower temperatures with increase of pressure. If

¹⁾ Die Heterogene Gleichgewichte 2, 139 (1904).

²⁾ These Proceedings Oct. 31, 1903, 439.

this case occurs, the *eutectic melting-point curve*, furnished by the system $A + B$ will generally present the same course. This case is rare.

As, however, BAKHUIS ROOZEBOOM already observed ¹⁾, a negative eutectic melting-point curve is also possible, when only the melting-point curve of one substance is negative, provided the negative course of one melting-point curve be stronger than the positive course of the other. To this belong all cryo-hydrate lines.

In the P, T -projection fig. 1 it has been assumed (which, however, is of minor importance here) that the negative course of the eutectic melting-point curve results from negative melting-point curves of the substances A and B .

The particularity attending the negative course of the eutectic melting-point curve, is this, that a p, x -section corresponding with a temperature below the eutectic point, will contain a region for $S_A + L$ and a region for $S_B + L$, separated by a liquid region L . The limits of this liquid region are given by solubility isotherms, which according to VAN DER WAALS' theory, are portions of two continuous curves indicating the fluid phases which can coexist with the solid substance A respectively B , and which have been called *de solubility isotherms*.

The regions for $S_A + G$ and $S_A + L$ resp. $S_B + G$ and $S_B + L$ below the eutectic point being separated by a region for $S_A + S_B$, the question which I wished to solve came to this: "what is the course of the two solubility isotherms in the region for $S_A + S_B$ ".

In order to answer this question we first examine what is the p, x -section which corresponds with a temperature above the eutectic point, but below the melting points of the two components. The temperature which I have chosen for this purpose, is denoted by t_1 in the P, T -projection. The p, x -section corresponding with this is represented in fig. 2. As VAN DER WAALS has proved that the solubility isotherm has two vertical tangents for the case $r_s < r_f$, but only one vertical tangent for the case $r_s > r_f$ two continuous solubility isotherms with one vertical tangent have been drawn in this p, x -section; for the one solubility isotherm this vertical tangent lies at the liquid point L , and for the other at the vapour point G . We see further that the branches which separate the liquid region L from the regions for $S_A + L$ and $S_B + L$ diverge towards higher pressure. The portion of the liquid-vapour-region $L + G$, which may be realized in stable condition, lies between the two three phase pressure lines $S_A GL$ and $S_B LG$. If we now examine a p, x -section,

¹⁾ Loc. cit. p. 418.

corresponding with the eutectic temperature, denoted by t_e in the P, T -projection, we get what is represented in fig. 2. The two three phase pressure lines $S_A + G + L$ and $S_B + L + G$ have both descended, the former, however, stronger than the latter, and they have finally coincided.

The two solubility isotherms intersect besides in the unstable region, also in the points G and L . While the point of intersection G indicates the possibility of a coexistence of $S_A + S_B + G$, the second point of intersection L indicates the possibility of a coexistence of $S_A + S_B + L$, and when at a definite temperature, as is the case here the two points lie on the same pressure line, this means that at that temperature the four phases $S_A + S_B + L + G$ can coexist, provided the pressure be equal to that indicated by the horizontal line which joins the four coexisting states. At a higher pressure the regions for $S_A + L$ and $S_B + L$ are separated by the triangular region for L .

In order to get a clear idea of the form which the px -section assumes at a temperature t_e , lying somewhat below the eutectic temperature, it is necessary to draw the metastable branches of the lines for $S_A + L_{AB} + G_{AB}$, for $S_B + L_{AB} + G_{AB}$ and for $L_A + G_A$, as has been done in fig. 1. We see then, that the situation of the first two three phase lines is just the reverse of that of the stable branches. For the stable branches that for $S_A + L_{AB} + G_{AB}$ lies, namely, above that for $S_B + L_{AB} + G_{AB}$, for the metastable branches the reverse is the case. If, taking this into consideration, we now draw the px -section corresponding with the temperature t_e , we get fig. 4, from which we see that the first point of intersection of the two solubility isotherms has moved upwards, and the second downwards. The first point of intersection denotes, as has been said, the coexistence of $S_A + S_B + G$, and the second the coexistence of $S_A + S_B + L$; at constant temperature these three phase equilibria are only possible at one pressure, because we have here a system of two components, hence for pressures between the two points of intersection mentioned there must be change of the three phase equilibria into a two phase system, where the two three phase pressure lines form the limits of a new *two phase region*, viz. for $S_A + S_B$.

The second point of intersection of the solubility isotherms which causes the occurrence of the three phases $S_A + S_B + L$ lies here in agreement with the dotted line traced in the P, T -projection for the temperature t_e at a pressure below that of the supercooled liquid of pure A .

It is further to be seen in this p, v -section, that the two metastable three phase pressure lines for $S_A + G + L$ and for $S_B + L + G$ lie above the stable three phase pressure line for $S_A + S_B + G$, and that the first lies between the two others. At the same time we see that the character of the solubility isotherms does not change, the only modification which is brought about for each of the isotherms compared with the usual case is this that the metastable part is enlarged.

If we now take a temperature which lies still somewhat lower, viz. t_4 , we get a p, v -section as represented in fig. 5. All the three phase pressure lines have diverged, and descended, except that for $S_A + S_B + L$, which has strongly ascended. The second point of intersection lies now, in agreement with what the dotted line for the temperature t_4 traced in the P, T -projection shows, far above the point indicating the vapour tension of the supercooled liquid of A . The metastable part of the two solubility isotherms has greatly increased, and with it the region for $S_A + S_B$. With further decrease of temperature the character of the modifications in the p, v -section remains the same, so that it is unnecessary to examine another.

If we had applied the same considerations to the case that the eutectic melting-point curve has a positive course, we should, with the exception of the unstable region, have found but one (lower) point of intersection for the solubility isotherms, for the branches which gave a second (higher) point of intersection in the case under discussion, recede continually from each other.

I have not represented this latter case, as it yields nothing special.

The case treated shows once more, how the examination of the equilibria which are hidden from our eyes, may contribute to widen our insight into those accessible to experiment.

Amsterdam, December 1905.

Anorganic Chemical laboratory of the University.

Chemistry. — “*On the phenomena which occur when the plaitpoint-curve meets the three phase line of a dissociating binary compound*”. By Dr. A. SMITS. (Communicated by Prof. H. W. BAKHUIS ROOSEBOOM).

1. In a previous paper¹⁾ I have already pointed out, that the interesting systems metal-oxygen, metal-hydrogen and metal-nitrogen, to which we may still add many of the systems metal-halogen, and metaloxide-acidanhydride, belong to the type ether-anthraquinone,

) Zeitschr. f. physik. chem. 51, 193 (1905).

but they are more complicated, because here the components may combine.

Now from a chemical point of view it is of the highest importance to examine also these more complicated phenomena, in order to obtain in this way a general insight into the phenomena of equilibrium for the case that compounds are raised to high temperatures, and placed under such a pressure that critical phenomena are found with saturated solutions. As yet any insight into this was wanting.

By bringing the results of my investigation on ether-anthraquinone in connection with the cases lately discussed by me in a paper: "Contribution to the knowledge of the PX and the PT-lines for the case that two substances enter into a combination which is dissociated in the liquid and the gas phase" ¹⁾, I have succeeded in arriving at a clear conception of the above mentioned phenomena.

In all the cases which I shall shortly discuss here, I start from the supposition that the compound under consideration is miscible with both components in fluid state in all proportions. On the whole our knowledge as to this is exceedingly slight, nor is there the least certainty on this head for the substances which I shall adduce here as examples.

2. First of all I shall consider the case, that two substances A and B yield a dissociating compound $A_m B_n$, the melting point of which lies above the critical temperature of the substance A. This case is met with in the system $\text{CaO}-\text{CO}_2$. If now the solubility of the compound $A_m B_n$ in A is still slight at the critical temperature of A, the continuous plaitpoint curve, which starts at the critical point of A (CO_2) and terminates in the critical point of B (CaO) will meet the solubility curve of $A_m B_n$ (CaCO_3) in fluid A (CO_2) in two points. That the point p exists has already been demonstrated by Dr. BÜCHNER ²⁾; in temperature this point lies only slightly above 31° , the solubility of CaCO_3 in fluid CO_2 being still very slight at this temperature.

This case has been represented in Fig. 1. The upper half of this diagram contains the projection of the spacial figure on the PT-plane; the lower half represents the projection of the *two phase regions* ³⁾ coexisting with solid substance, and the plaitpoint curve. The combination of these two projections seems to me the simplest way of

¹⁾ These Proc., June 1905, p. 200.

²⁾ Thesis for the doctorate, 106. (1905).

³⁾ At first I gave the name of *three phase regions* to these regions because, though they indicate only *two* phases, a third coexists with them. It seems, however, better to me to speak of *two phase regions coexisting with solid substance*, which term I shall use henceforth.

representation for a first investigation of these problems. For the sake of clearness I must draw attention to the fact, that in the T-X-projection the lines aE , E_p , qFE' and E'_c are the solubility curves, whereas aE_1 , E_1p , $qF'E_1'$ and $E_1'_c$ represent the vapour lines. In the P-T-projection, however, we get one *three phase line* for each pair of two corresponding lines for the liquid and gas phases coexisting with solid substance. These three phase lines are indicated by $A+L+G$, $A_m B_n + L+G$ and $B+L+G$ in the P-T-projection.

The first meeting of a solubility curve with the plaitpoint curve takes place in p and the second in q . According to VAN DER WAALS' theory a continuous transition from the solubility curve into the coexisting vapour curve takes place in these two points. If we take once more the system CO_2 — CaO as an example, p indicates the critical point of the saturated solution of $CaCO_3$ in fluid carbonic acid, and q the critical point of another solution saturated with $CaCO_3$, with a much larger concentration of $CaCO_3$.

Between these points p and q a fluid phase may occur alone or by the side of solid $A_m B_n (CaCO_3)$, and in the neighbourhood of these points the phenomenon of retrograde solidification must present itself. I will further emphatically point out here, that it is assumed, as is easily seen in the T-X-projection, that near the melting point the difference of the volatility of the components is not so large as to prevent the occurrence of a vapour of the composition of the compound. The point F' , where the composition of the vapour is the same as that of the compound, is the *maximum-sublimation point* and the point F , where the concentration of the liquid is the same as that of the compound, is the *minimum melting point*, or the melting point under the three phase pressure¹⁾. What I did not yet show in my previous paper is this that two lines start from the points F and F' , which pass continuously into each other at K . These lines form the continuous bounding curve of the two sheets of the PTX-surface for the composition of the compound. The continuous bounding curve touches the plaitpoint curve in K , so that K denotes the critical point of the dissociating compound. That this point K does not constitute a special point of the continuous plaitpoint curve is due to the fact that when the compound is assumed to dissociate, the critical point of the liquid compound does not essentially differ from that of the liquids with other compositions.

In fig. 1a the projection of the two phase regions coexisting with solid substance is represented, and also that of the plaitpoint curve

¹⁾ These Proc., June 1905, p. 200.

on the p - x -plane: further the solubility isotherms corresponding with the temperatures of the points p and q are indicated, from which the phenomenon of retrograde solidification appears clearly.

3. In the case discussed the situation of the points p and q depends on different properties of the compound and its components. In special cases it will, therefore, depend on this, on what part of the three phase line of the compound the point q lies. Undoubtedly there will be many cases where this point falls below the melting point. Probably this case will occur the sooner the more the volatility of the two components differs. In this paper, however, I continue to assume, that a vapour of the composition of the compound may exist.

In this different cases may present themselves, which each call for a separate discussion. So highly remarkable phenomena make e. g. their appearance, when the plaitpoint curve cuts the three phase line of the compound between the melting point and the maximum sublimation point. I shall, however, discuss this case and some others in another paper, and restrict myself now to the phenomena, which occur, when the point of intersection q , as has been drawn in Fig. 2, lies not only below the melting point of the compound, but also below the maximum sublimation point. *Also in this case the possibility is excluded that the compound melts, and the only way in which the solid compound can vanish, is by evaporation.*

The line for solid $A_m B_n + G$, which would touch the three phase line $A_m B_n + L + G$ in the maximum sublimation point, if this point existed, runs on uninterruptedly to infinity, at least when no further complications appear.

The T-X-projection occurring in fig. 2 may contribute to elucidate some points. As is to be seen there, the two phase region E', qE' coexisting with the solid compound, does not possess any liquid or vapour of the composition of the compound, which is in harmony with the supposition, that the points F and F' are wanting.

In fig. 2a I have traced the projection of the two phase regions coexisting with solid substance, and of the plaitpoint curve on the p - x -plane. Further there are some solubility isotherms in this diagram, which require a few words of explanation,

The curve $fGecf'$ denotes the solubility isotherm for a temperature somewhat below that of the point q . If we now consider the temperature of the point q , we get a solubility isotherm which touches in q , and which has two more points of inflection, as is indicated by the curve f, G, q, gf' . At a higher temperature we get a solubility isotherm, which does not touch any more, and from which the two points of inflection may disappear.

4. In the third place I will point out what I have already demonstrated in a previous publication ¹⁾, that when the tension of a compound is smaller at its melting point than that of the components, a three phase curve may occur with a very peculiar shape, viz with one minimum and two maxima.

Let us now consider the case that the melting point of this compound lies above the critical temperatures of the components, then the very peculiar phenomenon may present itself, that what occurred once in the system ether and anthraquinone, is here to be realized twice, and that the solubility curve which runs from one eutectic point to the other, meets the plaitpoint curve *four times*, which appears in the PT-projection fig. 3 as a four times repeated intersection of the three phase curve $A_mB_n + L + G$ and the continuous plaitpoint curve $bKLD$ in the points p, q, q' and p' .

It appears from the PT and TX-projections that for all possible concentrations a range of temperature may be pointed out, within which the solid compound can only coexist with a fluid phase. When, however, which is conceivable, the portions cut out of the three phase line have no range of temperature in common, the temperature regions for solid + fluid, lie above each other, and so we have no symmetrical phenomena for any temperature on both sides of the line for A_mB_n in the PT-projection.

The systems hydrogen-water and oxygen-water belong to the type ether-anthraquinone when the components are miscible in all proportions. Each of these systems will then yield a point p and a point q . Supposing, which is, however, highly improbable, that by the application of a catalyser we could bring about equilibrium between oxygen, hydrogen and water vapour at any temperature, we should get a continuous three phase line for ice + L + G as is indicated in fig. 3, and also one continuous plaitpoint curve. The equilibrium with water, however, lying theoretically almost quite on the side of water at lower temperatures, we should commit a practically unappreciable error, when we tried to realize at these lower temperatures the diagram drawn here by starting in one case from ice, resp. water + hydrogen, and in another case from ice, resp. water + oxygen.

This example, however, is not suitable for illustration of the assumed case, because for this purpose we require a compound which appreciably dissociates at its melting point. I have only mentioned the system H_2-O_2 to show how remarkable this system is.

It is very probable that systems are to be found, with which the

¹⁾ loc cit.

supposed case may be realized without excessive experimental difficulties. This may succeed with NH_3-HCl . A system for which fig. 3 holds, presents also this particularity, that we have here a P, T, X-surface of two sheets with a *minimum curve* bounded on the upper side by a continuous plaitpoint curve, which, in consequence of the great difference between the critical temperatures of the compound and the components might possibly have the shape described here.

Prof. VAN DER WAALS was so kind as to draw my attention to the particularities of the P, T, X-surface of two sheets, which may be derived directly from those of a surface with a maximum curve, by simply reversing everything. The minimum curve, i. e. the locus of all points for which the concentration of liquid and vapour are the same, forms here the lower boundary of the projection of the P, T, X-surface of two sheets on the P, T-plane. This curve is represented in fig. 3 by the dotted line LL' , which touches the plaitpoint curve at L , and the continuous three phase line at N . This point N , lying between the minimum M in the three phase line and the maximum sublimation point F , as I have shown in a paper forwarded to the Zeitschr. f. phys. Chem. towards the end of September, is a point where the concentration of the vapour is equal to that of the liquid, and is therefore at the same time a point of the minimum curve, which becomes metastable on the left of N . The peculiar feature in the P, T, X-surface of two sheets drawn here manifests itself, when the bounding curves are traced for different concentrations.

It appears then, that if we come from the side of B , the concentration of the point L is the first, at which the bounding curve presents some particularity. At this concentration we get, viz., two bounding curves, which starting from Q and S , terminate at L in a so-called cusp, as is here once more separately represented.



With a concentration somewhat richer in A we get now two bounding curves which pass continuously into each other. The continuous transition takes place where the bounding curve touches the plaitpoint curve. Further this continuous bounding curve shows this particularity that the two branches touch each other near the critical

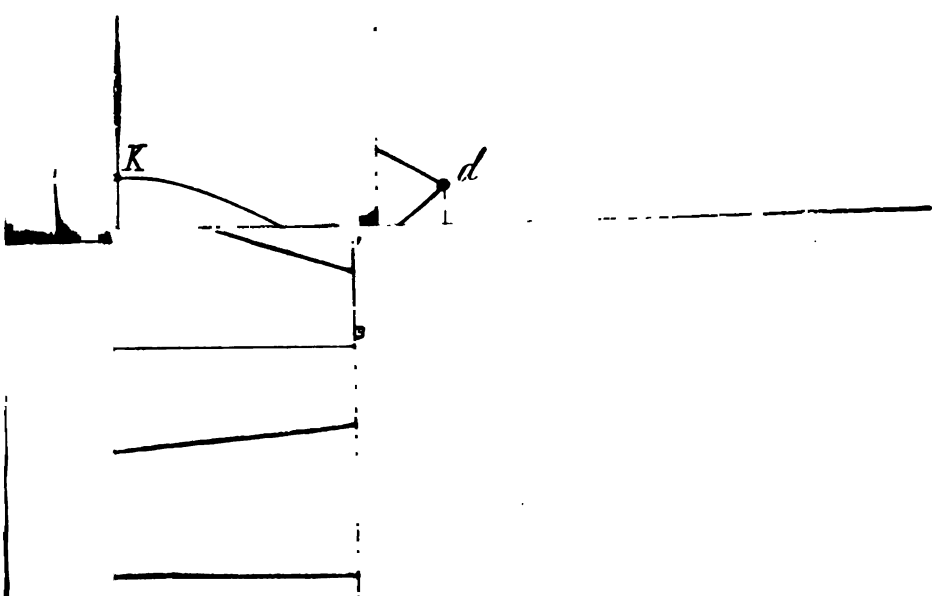


Fig. 3.

point, and form in this way a loop, as is separately represented below.



The point of tangency m lies on the minimum curve.

With concentrations still richer in A, the character of the bounding curves remains the same, only the point m shifts along the minimum curve towards N , so that, when we choose the concentration corresponding with the point N , the bounding curve gets this shape, where the vapour branch as well as the liquid branch touches the three phase line at N .



If we now pass on to greater concentration of A, we get again bounding curves of the usual form, for the point of tangency m lies now in the metastable region. If the critical point of the bounding curve, coincides with the maximum temperature of the plaitpoint curve then m lies at the absolute zero point. Leaving further particularities undiscussed, I will only just point out that the minimum curve, beyond the point N towards lower temperatures, lies below the three phase line, which is necessary, because the supersaturate solution has a smaller vapour tension than a saturate one and it is wanted for the realisation of the metastable branch of the minimum curve that the solid substance does not make its appearance.

Now as to the T-X-projection on fig. 3 we may still remark, that in accordance with the foregoing remark the liquid line $qF'Nq'$ cuts the vapour line $qFNq'$ in N at a temperature and pressure lying somewhat below that of the maximum sublimation point F' , but slightly above that of the minimum point M of the three phase line. In N vapour and liquid are therefore of the same concentration, but this is not the case at the minimum M .

In fig. 3a the projection is represented of the two phase regions coexisting with solid substance on the p,x -plane, which diagram does not call for further elucidation.

Amsterdam, December 1905.

Anorganic-Chemical-laboratory of the University.

Chemistry. — “On the course of the spinodal and the plaitpoint lines for binary mixtures of normal substances.” By J. J. VAN LAAR. (Third communication). (Communicated by Prof. H. A. LORENTZ).

1. In my last paper ¹⁾ on the above mentioned subject I discussed the general equations of the spinodal and the plaitpoint lines, viz. $RT = f(v, x)$ and $F(v, x) = 0$ (derived in a previous communication ²⁾) for the special case $b_1 = b_2$, i. e. $\pi = \theta$, when π denotes the ratio of the critical pressures $\frac{p_2}{p_1}$, and θ that of the critical temperatures $\frac{T_2}{T_1}$ of the components. (The higher critical temperature is always T_1).

I started from VAN DER WAAIS' equation of state, where b was assumed to be independent of v and T , while further in the quadratic equations :

$$\begin{cases} b = (1-x)^2 b_1 + 2x(1-x) b_{12} + x^2 b_2 \\ a = (1-x)^2 a_1 + 2x(1-x) a_{12} + x^2 a_2 \end{cases}$$

it was assumed that

$$b_{12} = \frac{1}{2}(b_1 + b_2) ; \quad a_{12} = \sqrt{a_1 a_2}, \quad (1)$$

which reduces the above expressions to

$$\begin{cases} b = (1-x) b_1 + x b_2 \\ a = ((1-x) \sqrt{a_1} + x \sqrt{a_2})^2 \end{cases}$$

Henceforward we shall indicate by the name *normal* (binary) *mixtures* such mixtures, the components of which are not only simple, but where *both* the relations (1) may be considered as satisfied.

The discussion in question led to the occurrence of *two separate branches* of the plaitpoint line (see plate loc. cit.), which present a *double point* at a definite value of θ (fig. 4). If $\theta < 2.89$ (when $b_1 = b_2$), we have the normal shape, represented in fig. 2; if $\theta > 2.89$, we find the abnormal shape, represented in fig. 1, which as yet has been only considered possible for mixtures, of which at least one of the components is associating (abnormal). ($C_2H_6 + CH_3OH$, $C_2H_6 + H_2O$, $SO_2 + H_2O$, Ether + H_2O).

The possibility of a third case was also briefly mentioned (see fig. 3), examples of which have been described inter alia by KUENEN ($C_2H_6 + C_2H_5OH$, etc.); but this case was not further discussed, nor the connodal relations and three phase equilibria, which, for the

¹⁾ These Proc., June 1905, p. 144.

²⁾ These Proc., April 1905, p. 646.

rest, were already known. (The chief points had already been previously described by KORTEWEG and VAN DER WAALS).

In a later paper¹⁾ the place of the double point, the knowledge of which is important, because it indicates the separation of two very different types, was determined for the perfectly general case $b_1 \gtrless b_2$, and the discussion of the shape of the plaitpoint line was extended to the case $\pi = 1$, i. e. to the case which is of frequent occurrence, that the critical pressures of the two components are equal. In this latter case it was inter alia found, that not before $\theta > 9,9$ the case of fig. 1 loc. cit. is found.

I further derived from the perfectly general expression :

$$RT = f(v, x) \quad ; \quad F(v, x) = 0$$

of the plaitpoint line also the initial course, viz. $\frac{1}{T_1} \left(\frac{dT_x}{dx} \right)_0$ ²⁾, chiefly in connection with opinions expressed previously on this point.

As I remarked before (loc. cit. p. 34), VAN DER WAALS had already drawn up the *differential* equation of the plaitpoint line, and drawn a series of general conclusions from it. Also in a few papers of very recent date³⁾ he has demonstrated in his own masterly way how far we may get with general *thermodynamical* considerations and *general* relations, derived from the equation of state. But seeing that VAN DER WAALS himself in his Ternary Systems IV (These Proc. V, p. 1—2) with perfect justice emphatically points out the absurdity of the often prevailing opinion as if an equation of state should not be required for the knowledge of the binary systems, I have considered it not unprofitable to transform the *differential* equation of the plaitpoint line, viz. $\frac{\partial f}{\partial x} + \frac{\partial f}{\partial v} \left(\frac{\partial v}{\partial x} \right)_{pT}$, where f represents the second member of $RT = f(v, x)$ — the equation of the spinodal lines — by means of the equation of state into a *finite* relation $F(v, x)$, which in combination with $RT = f(v, x)$ expresses the plaitpoint line in the usual data T, v, x . This enabled me to get acquainted with new particulars concerning its course (inter alia its splitting up into two separate branches), and to examine this course in its details more closely

¹⁾ Arch. TEYLER (2) X, Première partie, p. 1—26 (1905).

²⁾ These Proc. VIII, p. 144.

³⁾ These Proc. VIII, p. 271—298. The first mentioned paper was cited by me (loc. cit. p. 34), so it has by no means "been overlooked", that already ten years ago VAN DER WAALS determined the principal properties of the critical line. (cf. v. D. WAALS loc. cit. p. 271).

than has been done up to now. I also pointed out (loc. cit. p. 15) that already before me KORTEWEG has tried to find a finite expression for the plaitpoint line, but has not fully succeeded in this. His discussion extends after all only over the special case¹⁾ $b_1=b_2=b_{12}$, $a_1=a_2$ (but $a_{12}=\kappa a_1$), whereas in my paper cited it was assumed in the discussion that $b_1=b_2$, but that $a_1 \geq a_2$ (and $a_{12}=\sqrt{a_1 a_2}$). KORTEWEG's paper is of the highest importance, specially with regard to the connodal relations, which are often so intricate, and to which we shall presently come back.

The equation of the plaitpoint line once being derived in the above mentioned finite form, it was hardly any difficulty to derive also for the expression $\frac{1}{T_1} \left(\frac{dT_x}{dx} \right)_0$ on the side of lower critical temperature an accurate expression, in which *only* the quantities $\theta = \frac{T_2}{T_1}$ and $\pi = \frac{p_2}{p_1}$ occur. In VAN DER WAALS' paper mentioned by me in the paper cited, again only the general *differential* equation for the expression mentioned is given. (cf. (9) p. 89).

2. Some important points are left for discussion.

1st The discussion of the transition case at the *double point*, with regard to the shape of the spinodal lines etc; and the discussion of the possibility of the 3rd case (loc. cit. fig. 3).

2nd The treatment of the special case $\theta = 1$.

3rd The different connodal relations in the three chief cases and in the transition case.

4th The particularity of the *cusp* at R_1 , R_2 and R_3' in the p, T -representations of the three cases (loc. cit. 1a, 2a and 3a).

5th The question concerning the occurrence of a *minimum* critical temperature, and in connection with this of a *maximum* vapour pressure.

Let us in accordance with our last paper (loc. cit. p. 144) begin with the fifth point.

a. *Minimum-critical temperature.*

In this paper I derived the formula:

$$\frac{1}{T_1} \left(\frac{dT_x}{dx} \right)_0 = \Delta = \theta \sqrt{\frac{1}{\pi}} \left[\theta \sqrt{\frac{1}{\pi}} \left(\frac{1}{2}, -\frac{1}{2}, \sqrt{\frac{1}{\pi}} \right)^2 - 1 \right]. \quad (2)$$

¹⁾ Arch. Néerl. 24 (1891), p. 297, 324, 337 and 341.

Putting $\Delta < 0$, we get:

$$\theta \sqrt{\frac{1}{\pi}} \left(\frac{1}{2} - \frac{1}{2} \sqrt{\frac{1}{\pi}} \right)^2 - 1 < 0,$$

i. e.

$$\theta < \frac{\sqrt{\pi}}{\left(\frac{1}{2} - \frac{1}{2} \sqrt{\frac{1}{\pi}} \right)^2},$$

or

$$\theta < \frac{4\pi\sqrt{\pi}}{(3\sqrt{\pi}-1)^2} \dots \dots \dots (3)$$

This gives the following synopsis:

$\pi = \frac{1}{16}$	$\frac{1}{16}$	$\frac{1}{4}$	$\frac{1}{4}$	1	4	9	16	25
$\theta < \frac{1}{16}$	1	∞	2	1	$1\frac{1}{16}$	$1\frac{1}{4}$	$2\frac{1}{16}$	$2\frac{1}{4}$

θ always being assumed ≥ 1 (T_1 is the lower of the two critical temperatures), a minimum critical temperature can only occur, when π , i. e. the ratio of the two critical pressures $> \frac{1}{16}$.

If $\pi = \frac{1}{16}$, this takes place for *all* values of θ ; if $\pi = \frac{1}{4}$, only for values of θ between 1 and 2; etc. etc. (For $\pi = 1$, a minimum occurs in the above series of extreme values for θ , viz. $\theta = 1$). Now in by far the most cases π will probably lie between 1 and 4, so that θ will always have to be quite near 1, if a minimum critical temperature is to be found.

Let us take as an illustration the normal substances C_3H_8 and N_2O , investigated by KUENEN. There

$$\pi = \frac{74}{45} = 1,65, \quad \sqrt{\pi} = 1,29, \quad \theta = \frac{273 + 36}{273 + 35} = 1,00.$$

According to the above rule, θ has to be smaller than 1,04, if T_x is to be minimum. This is the case here. KUENEN found really a minimum value for T_x .

We also call attention to the fact that when $\underline{b_1 = b_2}$, so $\underline{\pi = \theta}$, no value of θ exists > 1 satisfying the inequality (3). For $\theta = \pi = 1$ ($\underline{a_1 = a_2}$, $\underline{b_1 = b_2}$) the two members are equal, and the line of the critical temperatures is a straight line. The foregoing is in perfect concordance with what we have derived in a previous paper with regard to this point (loc. cit. p. 43).

Also in the special case $\underline{\pi = 1}$ evidently *not a single* value of θ exists greater than 1, which satisfies (3). But in the case $\underline{\theta = 1}$ there is *always* a value of π conceivable, yielding a minimum for

T_r . Evidently in this case $\sqrt{\pi}$ must be greater than $1/4$, as

$$4(\sqrt{\pi})^3 - 9(\sqrt{\pi})^2 + 6\sqrt{\pi} - 1 = (\sqrt{\pi} - 1)^2 (4\sqrt{\pi} - 1),$$

and hence $\pi > 1/16$, in agreement with what has already been found above.

b. Maximum of vapour pressure. As is known, this will occur at higher temperatures, when at lower temperatures in the case of a three phase equilibrium the three phase pressure does not lie between the vapour pressures of the two components, but is greater than either. The concentration x_2 of the vapour lies then *between* the concentrations x_1 and x_3 of the two liquid phases. On the side of the lower critical temperature $x_2 > x_1$ will always have to be satisfied.

Let us now try to determine the condition for this.

For equilibrium between the phase 1 and 3 we have evidently when μ_a and μ_b represent the molecular potentials of the two components:

$$(\mu_a)_1 = (\mu_a)_3 \quad ; \quad (\mu_b)_1 = (\mu_b)_3,$$

or

$$\left. \begin{aligned} C_a - \left(\Omega - x \frac{\partial \Omega}{\partial x} \right)_1 + RT \log(1 - x_1) &= C_a - \left(\Omega - x \frac{\partial \Omega}{\partial x} \right)_3 + RT \log(1 - x_3) \\ C_b - \left(\Omega + (1 - x) \frac{\partial \Omega}{\partial x} \right)_1 + RT \log x_1 &= C_b - \left(\Omega + (1 - x) \frac{\partial \Omega}{\partial x} \right)_3 + RT \log x_3 \end{aligned} \right\},$$

where $\Omega = \int p dv - pv$, and C_a and C_b are functions of the temperature.

Subtraction of the two equations yields:

$$\frac{\partial \Omega}{\partial x_1} + RT \log \frac{1 - x_1}{x_1} = \frac{\partial \Omega}{\partial x_3} + RT \log \frac{1 - x_3}{x_3},$$

or

$$\log \frac{1 - x_1}{x_1} \frac{x_3}{1 - x_3} = \frac{1}{RT} \left[\frac{\partial \Omega}{\partial x_3} - \frac{\partial \Omega}{\partial x_1} \right],$$

as has been repeatedly derived before, *inter alia* by VAN DER WAALS.

Now we found before for $\frac{\partial \Omega}{dx}$ (l.c. p 649 formula (3) and p. 650):

$$\frac{\partial \Omega}{\partial x} = \frac{2\sqrt{a}}{v} (\sqrt{a_2} - \sqrt{a_1}) - \left(p + \frac{a}{v^2} \right) (b_2 - b_1).$$

Hence we have for $x = 0$, when $a = a_1$:

$$\left(\frac{\partial \Omega}{\partial x_2} - \frac{\partial \Omega}{\partial x_1} \right)_{x=0} = 2\sqrt{a_1} (\sqrt{a_2} - \sqrt{a_1}) \left(\frac{1}{v_2} - \frac{1}{v_1} \right) - a_1 (b_2 - b_1) \left(\frac{1}{v_2^2} - \frac{1}{v_1^2} \right),$$

so that we get at *low* temperatures (when $\frac{1}{v_2}$ and $\frac{1}{v_1}$ may be neglected and $v_1 = b_1$ may be put):

$$\left(\log \frac{x_2}{x_1} \right)_{x=0} = \frac{1}{RT} \left[\frac{a_1(b_2 - b_1)}{b_1^2} - \frac{2\sqrt{a_1}(\sqrt{a_2} - \sqrt{a_1})}{b_1} \right] \quad (4)$$

From this we see already, that when $b_2 = b_1$ ($\pi = \theta$), so $\sqrt{a_2} > \sqrt{a_1}$ (because θ must be larger than 1), then $\left(\log \frac{x_2}{x_1} \right)_0$ is always *negative*, i.e. $x_2 < x_1$. Hence just as little a three phase pressure $>$ than the two vapour branches, as a minimum critical temperature.

Let us now proceed to derive the condition for $x_2 > x_1$ from (4).

Then (dividing by $\frac{\sqrt{a_1}}{b_1}$) we must get:

$$\frac{\sqrt{a_1}}{b_1} (b_2 - b_1) > 2(\sqrt{a_2} - \sqrt{a_1}),$$

i. e.

$$\frac{b_2}{b_1} - 1 > 2 \left(\frac{\sqrt{a_2}}{\sqrt{a_1}} - 1 \right),$$

or as $\frac{b_2}{b_1} = \frac{\theta}{\pi}$ and $\frac{\sqrt{a_2}}{\sqrt{a_1}} = \frac{\theta}{\sqrt{\pi}}$:

$$\frac{\theta}{\pi} + 1 > 2 \frac{\theta}{\sqrt{\pi}},$$

from which follows:

$$\theta < \frac{\pi}{2\sqrt{\pi} - 1} \quad (5)$$

Hence this condition is another than the condition (3) for the minimum critical temperature, and we shall at once examine in how far the two conditions include or exclude each other.

No more than for $\pi = \theta$ does a value of θ satisfy the above inequality for $\pi = 1$. If $\theta = 1$, then, provided $\sqrt{\pi} > \frac{1}{2}$, $\pi - 2\sqrt{\pi} + 1$ must be > 0 ; and as this will always be satisfied, x_2 will be $> x_1$ for $\theta = 1$ on the side of the first component, when $\pi > \frac{1}{4}$. (We found only then a minimum critical temperature for $\theta = 1$, when $\pi > \frac{1}{16}$).

We can now easily prove, that always:

$$\frac{4\pi\sqrt{\pi}}{(3\sqrt{\pi}-1)^2} < \frac{\pi}{2\sqrt{\pi}-1},$$

when $\pi > \frac{1}{4}$. For the above leads to:

$$(3\sqrt{\pi}-1)^2 > 4\sqrt{\pi}(2\sqrt{\pi}-1),$$

i. e. to $\pi - 2\sqrt{\pi} + 1 > 0$, which is again always satisfied.

Hence we have for $\pi > \frac{1}{4}$:

If there is a minimum critical temperature, then also $x_2 > x_1$ (but not necessarily *vice versa*); if not $x_2 > x_1$, then there is no minimum of T_x . (Again the reverse need not be true).

If π should be $< \frac{1}{4}$, then never $x_2 > x_1$, while T_x is only minimum, when (3) is satisfied, viz. if $\pi > \frac{1}{14}$. But this exceptional case, viz. that for $\theta > 1$ the value of π remains below $\frac{1}{4}$, will be very rare.

It appears therefore convincingly from the above, that the two conditions include each other often, but by no means always.

Just one example: *Ether* + H_2O .

Here $\theta = \frac{273 + 364}{273 + 195} = 1,36$, $\pi = \frac{195}{36} = 5,42$, $\sqrt{\pi} = 2,35$. The

second member of (3) becomes therefore $= \frac{51,0}{36,6} = 1,39$. As therefore

$\theta < 1,39$, there will be a minimum critical temperature, and hence also $x_2 > x_1$ according to the above rule. In fact the second member of (5) = 1,46, and θ being $< 1,39$, so a fortiori $\theta < 1,46$.

What is found, is in harmony with experiment, as the three phase pressure was found larger than the vapour pressure of ether.

Let us now take C_2H_6 + H_2O .

Here the three phase pressure was found *smaller* than that of C_2H_6 . Let us now examine if the inequality of (5) predicts the same. As

$\theta = \frac{273 + 364}{273 + 35} = 2,07$, $\pi = \frac{195}{45,2} = 4,31$, $\sqrt{\pi} = 2,08$, so we find

for $\frac{\pi}{2\sqrt{\pi}-1}$ the value 1,36. And so 2,07 is *not* $< 1,36$ now. Here too the rule holds again.

According to the above rule there is now *not* a minimum critical temperature either. The second member of (3) becomes now $\frac{35,9}{27,5} = 1,31$, and 2,07 is still less $< 1,31$ than $< 1,36$.

The two examples are illustrations of the *first* principal type, where a plaitpoint curve runs from C_1 to A , and one from C_2 to C_3 .

The reader will observe, that *water* serves here as 2nd component, so a very abnormal substance. But we must bear in mind, that in the neighbourhood of $x = 0$, where both the rules hold, the liquid phase consists *almost entirely* of *ether* (resp. C_2H_6), so that the *water* present may be considered as almost perfectly normal on account of the extremely high degree of dilution.

For the sake of completeness we mention that two other known examples, which with those mentioned are about the only ones

known, or rather investigated, which belong to Type 1, both follow the rule derived.

With $C_2H_6 + CH_3OH$ θ is viz. 1.69, $\pi = 1.63$, so on account of $\pi = \theta$, x_2 cannot be $> x_1$. And with $SO_2 + H_2O$, $\theta = 1.49$, $\pi = 2.47$, $\sqrt{\pi} = 1.57$, hence the second member of (5) = 1.15. And 1.49 is not < 1.15 , so x_2 is also not $> x_1$. This implies again that no minimum critical temperature is found.

So the fact that of the four mixtures $C_2H_6 + CH_3OH$, $C_2H_6 + H_2O$, $SO_2 + H_2O$ and ether + H_2O only the last has a three phase pressure greater than the vapour pressures of the two components, is in perfect harmony with the theoretical derivations given above.

3. Let us now briefly discuss the *third* point, viz. the connodal relations. As we are guided by the different figures of the adjoined plate, a few words will suffice. The essential part was already given by me in a few suggestions in one of my last papers (loc. cit. p. 37 at the foot and p. 38 at the top; p. 44 at the foot and p. 45 at the top; p. 48 in the middle), where I referred to KORTEWEG's well-known papers, with regard to the neighbourhood of the points R_1 and R_2 , and to some papers by VAN DER WAALS, with regard to the points R_1 and R' , with the third principal type.

Now we may add to this, that recently VAN DER WAALS [in the Proceedings of the same Meeting as in which my first paper on the spinodal and the plaitpoint lines was published (Meeting of March 25 1905)] has given an addition to his former considerations concerning the just mentioned third type, in agreement with what KORTEWEG derived for this case already 14 years ago (loc. cit. p. 316—318, figs. 30—35). We have reproduced this course of transformation in our figs. 9, 10 and 11, but now in connection with our former considerations on the course of the plaitpoint line. So also in other cases.

a. *Principal type I* (figs. 1—6).

In fig. 1 we see the gradual transformation of the principal (transverse) plait, when the temperature falls from $\tau = \frac{T}{T_0} = 2.37$ at C_2 to 0.80. (These numerical values relate to special case $b_1 = b_2$, but when $b_1 < b_2$ the relations are modified only *numerically*, as I have demonstrated in the above cited paper in the Arch. Teyler). T_0 is the temperature of the point C_0 , and is put $= 1$. $\theta = \frac{T_2}{T_1}$

is here $= 4$. (cf. for these and other data the already repeatedly mentioned paper in these proceedings).

The plaitpoint P has strongly shifted to the side of the small volumes; there is always equilibrium between a gas phase 3 and a liquid phase 2, which is comparatively rich in the 2nd component. With smaller volumes the gas phase 3 is practically equal to a liquid phase, but the transition is gradual. (The full-traced border curves of the plaits in their v, x -projection, on which the straight node lines rest, represent everywhere the connodal lines; the dotted lines always represent the spinodal curves; the plaitpoint line is indicated by crosses).

At $\tau = 1,6$ and $\tau = 1$ we see the connodal lines in the figure. If τ is somewhat below 1, e.g. 0,98, a connodal line arises running at a short distance round C_0 , while the large connodal line shifts its plaitpoint further to C_0 . At $\tau = 0,97$ the two plaits meet in a *homogeneous double point*¹⁾. At still lower temperatures we have an open plait, of which the two branches of the connodal line recede towards the right and the left, and which is traced for $\tau = 0,8$. Up to the highest pressures, x_1 and x_2 continue to differ, and it is no longer possible to mix the two phases to one homogeneous liquid phase by pressure, however great. With values of T between T_0 and $0,97T_0$ the homogeneity reached at a certain high pressure was again broken at still higher pressure, after which the two phases diverge more and more up to a certain limit.

In fig. 2 an important moment has been represented. At $\tau = 0,63$ the spinodal curve *touches* namely the plaitpoint line C_1A in R_1 , and from this moment a new closed connodal line begins to appear of the shape as is represented in fig. 3 ($\tau = 0,62$) *within* the connodal line proper. The spinodal line touches that isolated curve twice, i.e. in the plaitpoints p and p' [all this has been fully explained by KORTEWEG (loc. cit.)], which for $\tau = 0,63$ coincide to a so-called "*point double hétérogène*" in R_1 ²⁾. The connodal line in question does not yet present, however, realizable equilibria, because that line lies on the ψ -surface *above* the tangent plane to the connodal line proper, which determines the phases 3 and 2.

¹⁾ In fig. 1 the spinodal lines seem to touch each other in this double point; of course this has to be an intersection.

²⁾ It need hardly be mentioned, that every time only one, after the contact at R_1 two points of the plaitpoint line correspond with the temperature of the spinodal and connodal line under consideration. All the other points of the plaitpoint line which is every time projected as a whole, belong to other, lower and higher temperatures.

Fig. 3a gives an enlarged, schematical representation of that isolated connodal line, where some straight lines represent the "hidden", non-realizable equilibria. The points a and a' , and in the same way b and b' are corresponding points. The "tail" at b' is always directed towards the side of the plaitpoint (which has already disappeared in our diagram) of the principal plait, the "point" at a lies on the opposite side.

We point out that the shape of the spinodal line, as is drawn in figs. 3 and 3a, implies, that it touches the plaitpoint line in the peculiar way, indicated in fig. 2. In the immediate neighbourhood of R_1 the uppermost portion lies left of the common tangent, the lowermost portion on its *right*.

At somewhat lower temperatures, in our example at $\tau = 0,61$ (fig. 4), the isolated connodal line begins to *touch* (in M) the connodal line proper, and from this moment one of the two new plaitpoints, viz. p , will become the plaitpoint of a new branch plait, which has thus arisen from the principal plait in the way described above. Cf. e. g. fig. 5, where $\tau = 0,60$. The point p' is always unrealizable, and this continues so down to the absolute zero, where the plaitpoint line terminates in A . On the other hand all the plaitpoints P from M to C_1 will form realizable plaitpoints of the new plait.

In fig. 4 phase 3 begins to split up into two new phases, the gas phase proper 3, and a new liquid phase 1, rich in the 1st component of the mixture. There is a three phase *line*, the beginning of a three phase *triangle* (see fig. 5), which continues to exist from this point down to the lowest temperatures.

In fig. 5 it is also seen how the connodal line which passed on uninterruptedly before, but which is now broken off in the angles 1 and 3 of the three phase triangle, proceeds on the ψ -surface. With this corresponds the well-known "ridge" on the connodal line at 2.

At $\tau = 0,59$ the new plaitpoint P reaches the lower critical temperature C_1 , and from this moment the branch plait is always open on the side $x = 0$, and this continues so down to the lowest temperatures.

The p, x -representations are omitted for want of space.

Fig. 6 gives the p, T -diagram of the plaitpoint lines. Noteworthy is, that we meet with a *cusp* in the line C_1A at R_1 , where the spinodal line *touches* the plaitpoint line (cf. fig. 2). We shall prove this further on. As we have already shown in our former paper, the pressure p approaches $-27 p_1$ at A , where $T = 0$. (This derivation holds

evidently also for the general case that $b \geq 0$). Comparison with fig. 4 teaches us, that the point M , where the three phase pressure begins, lies at a temperature *lower* than that of R_1 . If the three phase pressure lies between the vapour pressures of the two components (the full-traced curves starting from C_1 and C_2 represent the vapour tension lines), in other words if $x_1 > x_2$, then fig. 6 holds; if on the other hand $x_2 > x_1$ and the three phase pressure always higher than the vapour pressure of the two components, then fig. 6a holds. The line C_1R shows then a minimum. (In the figure the three phase pressure line is always denoted by $\Delta\Delta\Delta$).

b. *Principal type II.*

After what has been discussed above, the relations for this type may be made sufficiently clear even without diagrams. At a temperature somewhat lower than that of R_2 , where the spinodal line again touches the plaitpoint line (now C_2A) a three phase equilibrium again prevails. Now the gas phase 3 does not split up into 3 and 1, as with type I, but the liquid phase 2 into two liquid phases 2 and 1. Just as with type I the plaitpoints from M (between R_1 and C_1) to A were unrealizable (cf. also fig. 6), those from M (now between R_2 and C_2) to A are now also unrealizable. The three phase equilibrium formed continues to exist down to the lowest temperatures. Here the same phenomenon of the minimum critical temperature in the neighbourhood of C_2 is met with as with type I. At temperatures lower than $T = 0.96 T_0$ the two liquid phases 1 and 2 are no longer to be mixed to one homogeneous phase by pressure, however great.

The successive p, x -lines are again omitted.

Finally we find in fig. 7 the p, T -representation. The three phase pressure line lies here between the two vapour pressure lines, so that $x_2 < x_1$ on the border near $x = 0$.

c. *Principal type III.*

The possibility of this type for mixtures of *normal* substances will be examined separately afterwards. When it occurs (inter alia for mixtures of C_2H_6 with C_2H_5OH , etc., for triethylamine and water), then the plaitpoint line C_1C_2 has the shape drawn in fig. 8.

If we pass downward from the higher critical temperature at C_2 , a double plaitpoint will again occur at R_1 at the temperature indicated by t_1 , hence formation of an isolated connodal line as in fig. 3, at somewhat lower temperature. This goes on till at t_2 the closed

curve in M'' begins to get outside, i.e. outside the connodal line proper of the principal plait, at which the phase 3 begins to split up into 3 and 1 just as in fig. 4. This splitting up itself is represented at t_4 in fig. 9. A three phase equilibrium has formed then just as in fig. 5. The shape of the different connodal lines is still quite the same as in the analogous case in fig. 5, only the plaitpoint P of the principal plait had already disappeared there. This course has already been given by KORTEWEG, as was mentioned above, and VAN DER WAALS, too, has accepted it in one of his last papers (loc. cit.) on the transformation of a principal plait into a branch plait and the reverse.

The three phase equilibrium established is however not of long duration as we shall see. At still somewhat lower temperature t_5 a very interesting transformation takes place (see fig. 10), also mentioned by KORTEWEG (loc. cit. p. 318, fig. 34), and later by VAN DER WAALS (l.c.). The small letters a, b, c, d and a', b', c', d' placed in fig. 9 give a clear idea of the transformation.

Still somewhat lower, at t_7 (fig. 11), the plaits have reversed their functions; the branch plait of fig. 9 has become a principal plait, and reversely the principal plait has been transformed into a branch plait. We may notice that the "tail" at b is always turned to the side of the principal plait, both in fig. 9 and in fig. 11. Also the "ridge" has changed its place after the transition of fig. 10.

And then the further transformation resumes its normal course. There comes a moment, at t_8 (represented in fig. 8), that the isolated connodal line of fig. 11 begins to retreat within the connodal line proper of the principal plait. This takes place in M' , and the three phase equilibrium, which accordingly has been of very short duration, finishes. The two phases 1 and 2 have again coincided, and after this we have only coexistence of 3 and 2, as before, and as with type II before M in the neighbourhood of R_2 . The plaitpoint P of the principal plait continues to exist for some time more, but will soon also disappear (at C_1) ¹⁾ Also the closed connodal line remains past M' still for a short time within the connodal line proper, gets smaller and smaller, and disappears at last at R_2' , where the spinodal line touches the plaitpoint line once more (fig. 8 at t_9). The temperature t_{10} is the lower critical temperature of the two components, that of C_1 , and at still lower temperatures we begin gradually to approach the second plaitpoint line C_0A .

¹⁾ The temperature of R_2 (and M') may also be lower than that of C_2 . This really occurs for the above mentioned mixtures. The point P of the principal plait has then already disappeared before 1 and 2 coincide at M' .

At t_{11} contact of a spinodal line and the plaitpoint line takes place for the third time, viz. at the branch C_1A mentioned. Again at somewhat lower temperature a three phase equilibrium will be found at M by the repeated splitting up of 2 into 1 and 2, and now for good and all, down to the lowest temperatures. All this is quite identical with the case treated with type II.

Theoretically of importance for this remarkable third (very abnormal) principal type is therefore this, that after the two liquid phases 1 and 2 have become identical at M' (t_s), there *must* again take place splitting up of the homogeneous liquid phases into two separate phases with sufficient lowering of the temperature, viz. at M , somewhat below R_s (cf. also fig. 12).

We point out that the point M in fig. 4 and 6, and in fig. 7 is a so-called *upper* mixing-point, i.e. that at temperatures *higher* than the temperatures corresponding with that point the two phases 3,1 or 2,1 will form one homogeneous phase. The same thing is also the case for the points M and M'' of figs. 8 and 12. Above the temperature of M 1 coincides with 2, above that of M'' again 1 with 3. But the point M' is there a so-called *lower* mixing-point, for at temperatures *lower* than that of M' the phases 1 and 2, distinct at higher temperatures, coincide to one homogeneous phase.

For the plaitpoint line C_1C_2 of the third type (fig. 8) all the points, lying between M'' somewhat before R_1 and M' somewhat beyond R'_1 , are not to be realized. They form again the series of hidden plaitpoints p' , indicated in the figs. 9—11.

The p, x -representations are again omitted.

In the figs. 12 and 12a the p, T -representations of the plaitpoint line are drawn of the type mentioned. We again notice the three *cusps* R_1 , R_s and R'_1 . In fig. 12 the three phase pressure lies between the vapour pressures of the components; in fig. 12a above them. C_1R_1 has then again, as in fig. 6a, a retrogressive course.

We shall put off the discussion of the remaining points to a following paper. Those points are: *a.* The transition case between type I and II with the double point; *b.* the discussion of the possibility of the occurrence of type III; *c.* some remarks on the special case $\theta = 1$; *d.* the proof, that in the p, T -representations the different points R_1 , R_s and R'_1 are cusps.

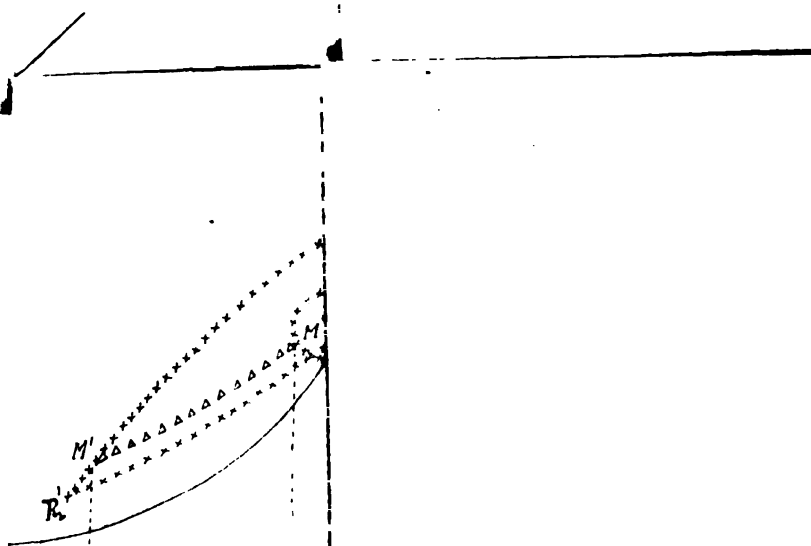


Fig. 12

Physics. — "*The absorption and emission lines of gaseous bodies.*"

By Prof. H. A. LORENTZ.

(Communicated in the Meetings of November and December 1905).

§ 1. The dispersion and absorption of light, as well as the influence of certain circumstances on the bands or lines of absorption, can be explained by means of the hypothesis that the molecules of ponderable bodies contain small particles that are set in vibration by the periodic forces existing in a beam of light or radiant heat. The connexion between the two first mentioned phenomena forms the subject of the theory of anomalous dispersion that has been developed by SELLMEYER, BOUSSINESQ and HELMHOLTZ, a theory that may readily be reproduced in the language of electromagnetic theory, if the small vibrating particles are supposed to have electric charges, so that they may be called electrons. Among the changes in the lines of absorption, those that are produced by an exterior magnetic field are of paramount interest. VOIGT ¹⁾ has proposed a theory which not only accounts for these modifications, the inverse ZEEMAN effect as it may properly be called, but from which he has been able to deduce the existence of several other phenomena, which are closely allied to the magnetic splitting of spectral lines, and which have been investigated by HALLO ²⁾ and GEEST ³⁾ in the Amsterdam laboratory. In this theory of VOIGT there is hardly any question of the mechanism by which the phenomena are produced. I have shown however that equations corresponding to his and from which the same conclusions may be drawn, may be established on the basis of the theory of electrons, if we confine ourselves to the simpler cases. In what follows I shall give some further development to my former considerations on the subject, somewhat simplifying them at the same time by the introduction of the notation I have used in my articles in the Mathematical Encyclopedia.

¹⁾ W. VOIGT, *Theorie der magneto-optischen Erscheinungen*. Ann. Phys. Chem. **67** (1899), p. 345; *Weiteres zur Theorie des ZEEMAN-effectes*, ibidem **68** (1899), p. 352; *Weiteres zur Theorie der magneto-optischen Wirkungen*. Ann. Phys., **1** (1900), p. 389. —

²⁾ J. J. HALLO, *La rotation magnétique du plan de polarisation dans le voisinage d'une bande d'absorption*, Arch. Néerl., (2), **10** (1905), p. 148.

³⁾ J. GEEST, *La double réfraction magnétique de la vapeur de sodium*, Arch. Néerl., (2), **10** (1905), p. 291.

⁴⁾ LORENTZ, *Sur la théorie des phénomènes magnéto-optiques récemment découverts* Rapports prés. au Congrès de physique, 1900, T. **3**, p. 1.

§ 2. We shall always consider a gaseous body. Let, in any point of it, \mathfrak{E} be the electric force, \mathfrak{H} the magnetic force, \mathfrak{P} the electric polarization and

$$\mathfrak{D} = \mathfrak{E} + \mathfrak{P} (1)$$

the dielectric displacement. Then we have the general relations

$$\frac{\partial \mathfrak{H}_z}{\partial y} - \frac{\partial \mathfrak{H}_y}{\partial z} = \frac{1}{c} \frac{\partial \mathfrak{D}_x}{\partial t}, \quad \frac{\partial \mathfrak{H}_x}{\partial z} - \frac{\partial \mathfrak{H}_z}{\partial x} = \frac{1}{c} \frac{\partial \mathfrak{D}_y}{\partial t},$$

$$\frac{\partial \mathfrak{H}_y}{\partial x} - \frac{\partial \mathfrak{H}_x}{\partial y} = \frac{1}{c} \frac{\partial \mathfrak{D}_z}{\partial t}, \quad . . . (2)$$

$$\frac{\partial \mathfrak{E}_z}{\partial y} - \frac{\partial \mathfrak{E}_y}{\partial z} = - \frac{1}{c} \frac{\partial \mathfrak{H}_x}{\partial t}, \quad \frac{\partial \mathfrak{E}_x}{\partial z} - \frac{\partial \mathfrak{E}_z}{\partial x} = - \frac{1}{c} \frac{\partial \mathfrak{H}_y}{\partial t},$$

$$\frac{\partial \mathfrak{E}_y}{\partial x} - \frac{\partial \mathfrak{E}_x}{\partial y} = - \frac{1}{c} \frac{\partial \mathfrak{H}_z}{\partial t}, \quad . . . (3)$$

in which c is the velocity of light in the æther.

To these we must add the formulæ expressing the connexion between \mathfrak{E} and \mathfrak{P} , which we can find by starting from the equations of motion for the vibrating electrons. For the sake of simplicity we shall suppose each molecule to contain only one movable electron. We shall write e for its charge, m for its mass and $(\mathbf{x}, \mathbf{y}, \mathbf{z})$ for its displacement from the position of equilibrium. Then, if N is the number of molecules per unit volume,

$$\mathfrak{P}_x = N e \mathbf{x}, \quad \mathfrak{P}_y = N e \mathbf{y}, \quad \mathfrak{P}_z = N e \mathbf{z} (4)$$

§ 3. The movable electron is acted on by several forces. First, in virtue of the state of all other molecules, except the one to which it belongs, there is a force whose components per unit charge are given by ¹⁾

$$\mathfrak{E}_x + \alpha \mathfrak{P}_x, \quad \mathfrak{E}_y + \alpha \mathfrak{P}_y, \quad \mathfrak{E}_z + \alpha \mathfrak{P}_z,$$

α being a constant that may be shown to have the value $1/2$, in certain simple cases and which in general will not be widely different from this. The components of the first force acting on the electron are therefore

$$e(\mathfrak{E}_x + \alpha \mathfrak{P}_x), \quad e(\mathfrak{E}_y + \alpha \mathfrak{P}_y), \quad e(\mathfrak{E}_z + \alpha \mathfrak{P}_z) (5)$$

In the second place we shall assume the existence of an elastic force directed towards the position of equilibrium and proportional to the displacement. We may write for its components

$$-f\mathbf{x}, \quad -f\mathbf{y}, \quad -f\mathbf{z}, \quad (6)$$

f being a constant whose value depends on the nature of the molecule.

¹⁾ LORENTZ, Math. Encycl. Bd. 5, Art. 14, §§ 35 and 36.

The equations may be further simplified, if, following a well known method, we work with complex expressions, all containing the time in the factor e^{int} . If we introduce the three quantities

$$\xi = f' - a - m' n^2, \dots \dots \dots (11)$$

$$\eta = n g', \dots \dots \dots (12)$$

and

$$\zeta = \frac{n \mathbf{H}}{c N e}, \dots \dots \dots (13)$$

the result becomes

$$\left. \begin{aligned} \mathfrak{E}_x &= (\xi + i \eta) \mathfrak{P}_x - i \zeta \mathfrak{P}_y, \\ \mathfrak{E}_y &= (\xi + i \eta) \mathfrak{P}_y + i \zeta \mathfrak{P}_x, \\ \mathfrak{E}_z &= (\xi + i \eta) \mathfrak{P}_z. \end{aligned} \right\} \dots \dots \dots (14)$$

§ 5. Before proceeding further, we shall try to form an idea of the mechanism by which the absorption is produced. It seems difficult to admit the real existence of a resistance proportional to the velocity such as is represented by the expressions (8). It is true that in the theory of electrons a charged particle moving through the æther is acted on by a certain force to which the name of resistance may be applied, but this force is proportional to the differential coefficients of the third order of $\mathbf{x}, \mathbf{y}, \mathbf{z}$ with respect to the time. Besides, as we shall see later on, it is much too small to account for the absorption existing in many cases; we shall therefore begin by neglecting it altogether, i. e. by supposing that a vibrating electron is not subject to any force, exerted by the æther and tending to damp its vibrations.

However, if, in our case of gaseous bodies, we think of the mutual encounters between the molecules, a way in which the regular vibrations of light might be transformed into an inordered motion that may be called heat, can easily be conceived. As long as a molecule is not struck by another, the movable electron contained within it may be considered as free to follow the periodic electric forces existing in the beam of light; it will therefore take a motion whose amplitude would continually increase if the frequency of the incident light corresponded exactly to that of the free vibrations of the electron.

In a short time however, the molecule will strike against another particle, and it seems natural to suppose that by this encounter the regular vibration set up in the molecule will be changed into a motion of a wholly different kind. Between this transformation and the next encounter, there will again be an interval of time during which a new regular vibration is given to the electron. It is clear that in this way, as well as by a resistance proportional to the velo-

city, the amplitude of the vibrations will be prevented from surpassing a certain limit.

We should be led into serious mathematical difficulties, if, in following up this idea, we were to consider the motions actually taking place in a system of molecules. In order to simplify the problem, without materially changing the circumstances of the case, we shall suppose each molecule to remain in its place, the state of vibration being disturbed over and over again by a large number of blows, distributed in the system according to the laws of chance. Let A be the number of blows that are given to N molecules per unit of time. Then

$$\frac{N}{A} = \tau$$

may be said to be the mean length of time during which the vibration in a molecule is left undisturbed. It may further be shown that, at a definite instant, there are

$$\frac{N}{\tau} e^{-\frac{\vartheta}{\tau}} d\vartheta$$

molecules for which the time that has elapsed since the last blow lies between ϑ and $\vartheta + d\vartheta$.

§ 6. We have now to compare the influence of the just mentioned blows with that of a resistance whose intensity is determined by the coefficient g . In order to do this, we shall consider a molecule acted on by an external electric force

$$a e^{int}$$

in the direction of the axis of x .

If there is a resistance g , the displacement \mathbf{x} is given by the equation

$$m \frac{d^2 \mathbf{x}}{dt^2} = -f \mathbf{x} - g \frac{d \mathbf{x}}{dt} + a e^{int},$$

so that, if we confine ourselves to the particular solution in which \mathbf{x} contains the factor e^{int} , and if we use the relation (7),

$$\mathbf{x} = \frac{a e}{m(n_0^2 - n^2) + i n g} e^{int} \dots \dots \dots (15)$$

In the other case, if, between two successive blows, there is no resistance, we must start from the equation of motion

$$m \frac{d^2 \mathbf{x}}{dt^2} = -f \mathbf{x} + a e^{int},$$

whose general solution is

$$\mathbf{x} = \frac{a e^{i n t}}{m(n_0^2 - n^2)} + C_1 e^{i n_0 t} + C_2 e^{-i n_0 t} \dots (16)$$

By means of this formula we can calculate, for a definite instant t , the mean value $\bar{\mathbf{x}}$ for a large number of molecules, all acted on by the same electric force $a e^{i n t}$. Now, for each molecule, the constants C_1 and C_2 are determined by the values of \mathbf{x} and $\frac{d\mathbf{x}}{dt}$ immediately after the last blow, i. e. by the values \mathbf{x}_0 and $\left(\frac{d\mathbf{x}}{dt}\right)_0$ existing at the time $t = \vartheta$, if ϑ is the interval that has elapsed since that blow. We shall suppose that immediately after a blow all directions of the displacement and the velocity of the electron are equally probable. Then the mean values of \mathbf{x}_0 and $\left(\frac{d\mathbf{x}}{dt}\right)_0$ are 0, and we shall find the exact value of $\bar{\mathbf{x}}$, if in the determination of C_1 and C_2 , we suppose \mathbf{x} and $\frac{d\mathbf{x}}{dt}$ to vanish at the time $t = \vartheta$.

In this way, (16) becomes

$$\mathbf{x} = \frac{a e^{i n t}}{m(n_0^2 - n^2)} \left\{ 1 - \frac{1}{2} \left(1 + \frac{n}{n_0} \right) e^{i(n_0 - n)\vartheta} - \frac{1}{2} \left(1 - \frac{n}{n_0} \right) e^{-i(n_0 + n)\vartheta} \right\}.$$

From this $\bar{\mathbf{x}}$ is found, if, after multiplying by $\frac{1}{\tau} e^{-\frac{\vartheta}{\tau}} d\vartheta$, we integrate from $\vartheta = 0$ to $\vartheta = \infty$. If u is an imaginary constant, we have

$$\frac{1}{\tau} \int_0^\infty e^{u\vartheta - \frac{\vartheta}{\tau}} d\vartheta = \frac{1}{1 - u\tau}.$$

Hence, after some transformations,

$$\bar{\mathbf{x}} = \frac{a e}{m \left(n_0^2 + \frac{1}{\tau^2} - n^2 \right) + 2 \frac{i m n}{\tau}} e^{i n t} \dots (17)$$

If this is compared with (15), it appears that, on account of the blows, the phenomena will be the same as if there were a resistance determined by

$$g = \frac{2 m}{\tau}, \dots (18)$$

and an elastic force having for its coefficient

$$(f) = f + \frac{m}{\tau^2} \dots (19)$$

Indeed, if the elastic force had the intensity corresponding to this formula, the square of the frequency of the free vibrations would have, by (7), the value $n_0^2 + \frac{1}{\tau^2}$. The equation (15) would then take the form (17).

In the next paragraphs the last term in (19) will however be omitted.

As to the time τ , it will be found to be considerably shorter than the time between two successive encounters of a molecule. Hence, if we wish to maintain the conception here set forth, we must suppose the regular succession of vibrations to be disturbed by some unknown action much more rapidly than it would be by the encounters.

We may add that, even if there were a resistance proportional to the velocity, the vibrations might be said to go on undisturbed only for a limited length of time. On account of the damping their amplitude would be considerably diminished in a time of the order of magnitude $\frac{m}{g}$. This is comparable to the value of τ which, by (18), corresponds to a given magnitude of g .

§ 7. The laws of propagation of electric vibrations are easily deduced from our fundamental equations. We shall begin by supposing that there is no external magnetic field, so that the terms with ζ disappear from the equations (14).

Let the propagation take place in the direction of the axis of z and let the components of the electromagnetic vectors all contain the factor

$$e^{in(t-qz)}, \dots \dots \dots (20)$$

in which it is the value of the constant q that will chiefly interest us. There can exist a state of things, in which the electric vibrations are parallel to OX and the magnetic ones parallel to OY , so that \mathcal{E}_x , \mathfrak{P}_x , \mathcal{D}_x and \mathfrak{H}_y are the only components differing from 0. Since differentiations with respect to t and to z are equivalent to a multiplication by in and by $-inq$ respectively, we have by (2) and (3)

$$q \mathfrak{H}_y = \frac{1}{c} \mathcal{D}_x, \quad q \mathcal{E}_x = \frac{1}{c} \mathfrak{H}_y.$$

Hence

$$\mathcal{D}_x = c^2 q^2 \mathcal{E}_x$$

and, in virtue of (1),

$$\mathfrak{P}_x = (c^2 q^2 - 1) \mathcal{E}_x.$$

The first of the equations (14) leads therefore to the following

formula, which may serve for the determination of q ,

$$c^2 q^2 - 1 = \frac{1}{\xi + i\eta} \quad \dots \quad (21)$$

Of course, q has a complex value. If, taking κ and ω real, we put

$$q = \frac{1 - i\kappa}{\omega}, \quad \dots \quad (22)$$

the expression (20) becomes

$$e^{i\kappa \left(t - \frac{1-i\kappa}{\omega} z \right)},$$

so that the real parts of the quantities representing the vibrations contain the factor

$$e^{-\frac{\kappa}{\omega} z} \quad \dots \quad (23)$$

multiplied by the cosine or sine of

$$\kappa \left(t - \frac{z}{\omega} \right).$$

It appears from this that ω may be called the velocity of propagation and that the absorption is determined by κ . If

$$\frac{\kappa}{\omega} = k,$$

(index of absorption), we may infer from (23) that, while the vibrations travel over a distance $\frac{1}{k}$, their amplitude is diminished in the ratio of 1 to $\frac{1}{e}$.

In order to determine ω and κ , we have only to substitute (22) in (21). We then get

$$\frac{c^2 (1 - i\kappa)^2}{\omega^2} = 1 + \frac{1}{\xi + i\eta},$$

or, separating the real and the imaginary parts,

$$\frac{c^2 (1 - \kappa^2)}{\omega^2} = 1 + \frac{\xi}{\xi^2 + \eta^2}, \quad \frac{2c^2 \kappa}{\omega^2} = \frac{\eta}{\xi^2 + \eta^2},$$

from which we derive the formulæ

$$2 \frac{c^2}{\omega^2} = \sqrt{\frac{(\xi + 1)^2 + \eta^2}{\xi^2 + \eta^2}} + \frac{\xi}{\xi^2 + \eta^2} + 1, \quad \dots \quad (24)$$

$$2 \frac{c^2 \kappa}{\omega^2} = \sqrt{\frac{(\xi + 1)^2 + \eta^2}{\xi^2 + \eta^2}} - \frac{\xi}{\xi^2 + \eta^2} - 1, \quad \dots \quad (25)$$

in which the radical must be taken with the positive sign.

If the different constants are known, we can calculate by these formulae the velocity and the index of absorption for every value of the frequency n ; in doing so, we shall also get an idea about the breadth and the intensity of the absorption band.

§ 8. In these questions much depends on the value of η . In the special case $\xi = 0$, i. e. if the frequency is equal to, or at least only a little different from that of the free vibrations, we have on account of (25)

$$2 \frac{c^2 \kappa^2}{\omega^2} = \sqrt{1 + \frac{1}{\eta^2}} - 1.$$

From what has been said above, it may further be inferred that along a distance equal to the wave-length in air, i. e. $\frac{2\pi c}{n}$, the amplitude decreases in the ratio of 1 to

$$e^{-\frac{2\pi c \kappa}{\omega}}$$

Now, in the large majority of cases, the absorption along such a distance is undoubtedly very feeble, so that $\frac{2\pi c \kappa}{\omega}$ must be a small number. The value of $\frac{c^2 \kappa^2}{\omega^2}$ must be still smaller and this can only be the case, if η is much larger than 1.

This being so, the radical in (25) may be replaced by an approximate value. Putting it in the form

$$\sqrt{1 + \frac{2\xi + 1}{\xi^2 + \eta^2}},$$

we may in the first place observe, that, since η is large, the numerator $2\xi + 1$ will be very small in comparison with the denominator, whatever be the value of ξ . Up to terms with the square of $\frac{2\xi + 1}{\xi^2 + \eta^2}$, we may therefore write for the radical

$$1 + \frac{1}{2} \frac{2\xi + 1}{\xi^2 + \eta^2} - \frac{1}{8} \frac{(2\xi + 1)^2}{(\xi^2 + \eta^2)^2}$$

and after some transformations

$$2 \frac{c^2 \kappa^2}{\omega^2} = \frac{4\eta^2 - 4\xi - 1}{8(\xi^2 + \eta^2)^2}.$$

As long as ξ is small in comparison with η^2 , the numerator of this fraction may be replaced by $4\eta^2$. On the other hand, as

soon as ξ is of the same order of magnitude as η^2 or surpasses this quantity, the fraction becomes so small that it may be neglected, and it will remain so, if we omit the term -4ξ in the numerator. We may therefore write in all cases

$$\frac{cx}{\omega} = \frac{\eta}{2(\xi^2 + \eta^2)},$$

so that the index of absorption becomes

$$k = \frac{n}{2c} \cdot \frac{\eta}{\xi^2 + \eta^2} \cdot \dots \dots \dots (26)$$

This formula shows that for $\xi = 0$ the index has its maximum value

$$k_0 = \frac{n}{2c\eta} \cdot \dots \dots \dots (27)$$

and that for $\xi = \pm v\eta$, it is $v^2 + 1$ times smaller.

The frequency corresponding to this value of ξ can easily be calculated. If α may be neglected, a question to which we shall return in § 18, (11) may be put in the form

$$\xi = m'(n_0^2 - n^2) \cdot \dots \dots \dots (28)$$

Hence, for $\xi = \mp v\eta$

$$m'(n^2 - n_0^2) = \pm v\eta = \pm vng',$$

or, on account of (10) and (18),

$$m(n^2 - n_0^2) = \pm vng = \pm \frac{2m\tau n}{\tau},$$

$$n^2 - n_0^2 = \pm \frac{2vn}{\tau}.$$

If $n - n_0$ is much smaller than n_0 , we may also write

$$n = n_0 \pm \frac{v}{\tau} \cdot \dots \dots \dots (29)$$

The preceding considerations lead to the well known conclusion, somewhat paradoxal at first sight, that the intensity of the maximum absorption increases by a diminution of the resistance, or by a lengthening of the time during which the vibrations go on undisturbed. Indeed, if g is diminished or τ increased, it appears by (10) and (12) that η becomes smaller and by (27) k_0 will become larger. This result may be understood, if we keep in mind that, in the case $n = n_0$, the one most favourable to "optical resonance", in molecules that are left to themselves for a long time a large amount of vibratory energy will have accumulated before a blow takes place. Though the blows are rare, the amount of vibratory energy which is converted into heat may therefore very well be large.

In another sense, however, the absorption may be said to be diminished by an increase of τ (or a diminution of g), the range of wave-lengths to which it is confined, becoming narrower. This follows immediately from the equation (26). Let a fixed value be given to ξ , so that we fix our attention on a point of the spectrum, situated at a definite distance from the place of maximum absorption, and let η be gradually diminished. As soon as it has come below ξ , further diminution will lead to smaller values of k , i. e. to a smaller breadth of the band.

If g is very small, or τ very large, we shall observe a very narrow line of great intensity.

§ 9. The observation of the bands or lines of absorption, combined with the knowledge that has been obtained by other means of some of the quantities occurring in our formulae, enables us to determine the time τ and the number N of molecules per unit volume.

I shall perform these calculations for two rather different cases, viz. for the absorption of dark rays of heat by carbonic dioxide and for the absorption in a sodium flame.

As soon as we know the breadth of the absorption band, or, more exactly, at what distance from the middle of the band the absorption has diminished in a certain ratio, the value of τ may be deduced from (29); we have only to remember that in this formula, n is the frequency for which the index of absorption is $\nu^2 + 1$ times smaller than the maximum n_0 .

ÄNGSTRÖM¹⁾ has found that in the absorption band of carbonic dioxide, whose middle corresponds to the wave-length $\lambda = 2,60 \mu$, the index of absorption has approximately diminished to $\frac{1}{2} k_0$ for $\lambda = 2,30 \mu$. This diminution corresponding to $\nu = 1$, we have by (29)

$$\frac{1}{\tau} = n - n_0,$$

if n_0 and n are the frequencies for the wave-lengths $2,60 \mu$ and $2,30 \mu$.

In this way I find

$$\tau = 10^{-14} \text{ sec.}$$

In the case of the absorption lines produced in the spectrum by a sodium flame, we cannot say at what distance from the middle the absorption has sunk to $\frac{1}{2} k_0$. We must therefore deduce the value of τ from the estimated breadth of the line. Though the value of ν corresponding to the border cannot be exactly indicated, we shall

¹⁾ K. ÄNGSTRÖM, Beiträge zur Kenntniss der Absorption der Wärmestrahlen durch die verschiedenen Bestandteile der Atmosphäre, Ann. Phys. Chem. **39** (1890), p. 267 (see p. 280).

In the case of the infra-red rays whose absorption has been measured by ÅNGSTRÖM we are probably concerned with the vibrations of charged atoms of oxygen or carbon. The mass of an atom of hydrogen being about $1,3 \times 10^{-24}$ gramme, I shall take

$$m = 2 \times 10^{-23}.$$

The result then becomes

$$N = 6 \times 10^{17}.$$

§ 11. The above method is not available for a sodium flame. HALLO has however observed that the value of N for this body may be deduced from his measurements of the magnetic rotation of the plane of polarization and GÆST has shown that the magnetic double refraction in the flame may serve for the same purpose. In what follows I shall only use one of HALLO's results.

In the first place it must be noticed that in the case to be considered, ξ is much larger and $\frac{\xi}{\xi^2 + \eta^2}$ much smaller than unity. The radical in (24) may therefore be replaced by

$$1 + \frac{\xi}{\xi^2 + \eta^2}$$

and the formula becomes

$$\frac{c}{\omega} = 1 + \frac{\xi}{2(\xi^2 + \eta^2)}.$$

Now, if there is an external magnetic field, the velocities of propagation ω_1 and ω_2 of right and left circularly polarized light can be calculated by a similar formula. We have only to replace ξ by $\xi - \zeta$ and by $\xi + \zeta$.¹⁾ From the results

$$\frac{c}{\omega_1} = 1 + \frac{\xi - \zeta}{2[(\xi - \zeta)^2 + \eta^2]} \quad \text{and} \quad \frac{c}{\omega_2} = 1 + \frac{\xi + \zeta}{2[(\xi + \zeta)^2 + \eta^2]}$$

we find for the angle of rotation per unit length

$$\varphi = \frac{1}{2} n \left(\frac{1}{\omega_1} - \frac{1}{\omega_2} \right) = \frac{n}{4c} \left\{ \frac{\xi - \zeta}{(\xi - \zeta)^2 + \eta^2} - \frac{\xi + \zeta}{(\xi + \zeta)^2 + \eta^2} \right\}. \quad (31)$$

In order to determine N by means of a measured value of φ , we begin by observing that, in virtue of the equation (28), for which we may write

$$\xi = 2 m' n_0 (n_0 - n),$$

each value of ξ determines a certain point in the spectrum whose distance from the middle of the band is proportional to ξ . At the

¹⁾ See LORENTZ, Sur la théorie des phénomènes magnéto-optiques, etc., § 16.

border of the band (if there is no magnetic field) ξ has the value $\nu \eta$, the coefficient ν being some moderate number, say between 3 and 6 (§ 9), and for one of the components of ZREMAN's doublet we have $\xi = \zeta$. In the magnetic field used by HALLO the distance of the components from the middle of the original line amounted to 0,15 A. E., half the breadth of the line being 0,5 A. E., as has already been said.

We have therefore the following relation between η and ζ :

$$\xi : \nu \eta = 0,15 : 0,5$$

$$\eta = \frac{3,3}{\nu} \zeta. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (32)$$

On the other hand, a point in the spectrum, at which the angle of rotation per unit length was approximately equal to unity, was situated at a distance of 1,6 A. E. $\left(\frac{35}{130} \right)$ of the mutual distance of the two D-lines) from the middle of the original line. This being 10 times the distance from this line to one of the components, we have approximately

$$\xi = 10 \zeta.$$

On substituting this value and (32) in the formula (31), it appears that the terms η^2 may be omitted. Hence, if (13) is taken into account,

$$\varphi = 0,005 \frac{n}{c \zeta} = 0,005 \frac{N \epsilon}{H}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (33)$$

or since $\varphi = 1$ is,

$$N \epsilon = 200 H.$$

The strength of the magnetic field in these experiments was 9000 in ordinary units, or

$$H = \frac{9000}{\sqrt{4 \pi}} = 2600$$

in those used in our equations. Taking for ϵ the value (30), I finally find

$$N = 4 \times 10^{14}.$$

§ 12. The value of η may likewise be calculated, both for the carbonic dioxide and for the sodium flame. In the first case we can avail ourselves of the formula (27), in which k_0 is now known; the result is

$$\eta = \frac{n}{2 c k_0} = \frac{\pi}{\lambda k_0} = 2,5 \times 10^4.$$

For the sodium flame we first draw from (33)

$$\zeta = 0,005 \frac{n}{c} = 0,01 \frac{\pi}{\lambda} = 500$$

and we then find by (32) the following limits for η
550 and 270.

These results fully verify our assumption that η would be a large number.

Finally we can compare the values we have found for τ with the period of the vibrations. In this way we see that in the flame some six or twelve thousand vibrations follow each other in uninterrupted succession. In the carbonic dioxyd on the contrary no more than a few vibrations can take place between two successive blows.

§ 13. After having found the number N of molecules in the sodium flame we can deduce from it the density d of the vapour of sodium. In doing so, I shall suppose the molecules to be single atoms, so that each has a mass equal to 23 times that of a mass of hydrogen. Taking for this latter $1,3 \times 10^{-24}$ gramme, I find

$$d = 12 \times 10^{-9}.$$

This is not very different from the number 7×10^{-9} found by HALLO.

HALLO has already pointed out that this value is very much smaller than the density of the vapour really present in the flame; at least, this must be concluded if we may apply a statement made by E. WIEDEMANN, according to which a certain flame with which he has worked contained per cm^3 . about 5×10^{-7} gramme of sodium. Perhaps the difference must be explained by supposing that only those particles that are in some peculiar state, a small portion of the whole number, play a part in the phenomenon of absorption. This would agree with the views to which LENARD has been led by his investigation of the emission by vapour of sodium.

It must be noticed that the value of N we have calculated for carbonic dioxyd warrants a similar conclusion. In the experiments of ÅNGSTRÖM the pressure was 739 mm. At this pressure and at 15°C . the number of molecules per cm^3 . may be estimated at $3,2 \times 10^{19}$. This is 50 times the number we have found in § 10.

§ 14. An interesting result is obtained if the time τ we have calculated for carbonic dioxyd is compared with the mean lapse of time between two successive encounters of a molecule. Under the circumstances mentioned at the end of § 13, the mean length of the free path is about 7×10^{-6} cm. The molecular velocity being 4×10^4 cm. per sec., this distance is travelled over in

$$1,8 \times 10^{-10} \text{ sec.},$$

i. e. in a time equal to 18000 times the value we have found for τ . We see in this way that it cannot be the encounters between molecules, by which the regular succession of vibrations comes to an end. It seems to be disturbed much more rapidly by some other cause which is at work within each molecule.

In the case of the sodium flame there is a similar difference between the length of time τ and the mean interval between two encounters.

§ 15. We shall now return for a moment to the resistance that has been spoken of in § 5, the only one that is really exerted by the aether. This resistance is intimately connected with the radiation issuing from a vibrating electron, and if a beam of light were weakened by its influence, this would be due to part of the incident energy being withdrawn from the beam and emitted again into the aether. Of course, this could hardly be called an absorption. But, apart from this objection, we can easily show that the resistance in question is much too small to account for the diminution of intensity that is really observed. Its component in the direction of x is

$$\frac{e^2}{6 \pi c^3} \frac{d^2 x}{dt^2},$$

or, for harmonic vibrations of frequency n ,

$$= \frac{n^2 e^2}{6 \pi c^3} \frac{dx}{dt}.$$

Comparing this with (8), we find

$$g = \frac{n^2 e^2}{6 \pi c^3}.$$

This amounts to $2,0 \times 10^{-21}$ for carbonic dioxyd (for the wavelength $\lambda = 2,60 \mu$ (§ 9)) and to $4,0 \times 10^{-20}$ in the case of the sodium flame. These numbers are far below those which result from (18), if we substitute the value that has been calculated for τ . We then get, for carbonic dioxyd $4,0 \times 10^{-9}$, and for the sodium flame a number between $1,2 \times 10^{-16}$ and $0,6 \times 10^{-16}$.

§ 16. It has already been shown in § 8 that an increase of η broadens the absorption band, diminishing at the same time the absorption in its middle. Indeed, in many cases we may say that the broader the band, the feebler is the absorption for a definite kind of rays.

The question now arises what is the total amount of energy

absorbed by a layer of given thickness z , if the incident beam contains all wave-lengths occurring in the part of the spectrum occupied by the absorption band. In treating this problem, I shall suppose the energy to be uniformly distributed over this range of frequencies, so that, if we write $I dn$ for the incident energy, in so far as it belongs to wave-lengths between n and $n + dn$, I is a constant.

The total amount of energy absorbed is then given by

$$A = I \int_0^{\infty} (1 - e^{-2kz}) dn. \quad . \quad . \quad . \quad . \quad . \quad (34)$$

Now, if the coefficient g and the time τ were independent of the density of the gas, both ξ and η would be inversely proportional to N ; this results from (10), (12) and (28). The equation (26) shows that under these circumstances and for a given value of n , k is proportional to N . The value of A will therefore be determined by the product Nz . This means that the total absorption would solely depend on the quantity of gas contained in a layer of the given thickness, whose boundary surfaces have unit of area; if the same quantity were compressed within a layer of a thickness $\frac{1}{2}z$, the absorption would not be altered.

The result is different, if g and τ depend on the density. In order to examine this point, I shall take z to be so small that $1 - e^{-2kz}$ may be replaced by $2kz - 2k^2z^2$, so that (34) becomes

$$A = 2I \left\{ z \int_0^{\infty} k dn - z^2 \int_0^{\infty} k^2 dn \right\} \quad . \quad . \quad . \quad . \quad . \quad (35)$$

Let us further confine ourselves to an absorption band, so narrow, that we may put

$$\xi = 2m'n_0(n_0 - n), \quad . \quad . \quad . \quad . \quad . \quad (36)$$

$$\eta = n_0 g', \quad k = \frac{n_0}{2c} \frac{\eta}{\xi^2 + \eta^2} \quad . \quad . \quad . \quad . \quad . \quad (37)$$

Introducing ξ , instead of n , and extending the integrations from $\xi = -\infty$ to $\xi = +\infty$, as may indeed be done, I find from (35)

$$A = \frac{\pi I}{2cm'} \left(z - \frac{1}{4cg'} z^2 \right),$$

or, on account of (10),

$$A = \frac{\pi I}{2cm} \left\{ Ne^2 z - \frac{1}{4cg} (Ne^2 z)^2 \right\}.$$

Two conclusions follow from this result. First, the absorption in an infinitely thin layer of given thickness does not depend on the

value of g . In the second place, if the layer is so thick that the second term in the formula has a certain influence, for a given value of Nz , the amount of absorption will increase with g . It will therefore increase by a compression of the gas, if by this means the coefficient g takes a larger value. An effect of this kind has really been observed by ÅNGSTRÖM¹⁾ in his experiments on the absorption produced by carbonic dioxide.

This result could have been predicted by theory if the idea that the succession of regular vibrations would be disturbed by the collisions between the molecules had been confirmed; then, by an increase of the density, the time τ would become shorter and the formula (18) would give a larger value for the coefficient g . As it is, the vibrations must be supposed to be disturbed by some other cause (§ 14) and we can only infer from ÅNGSTRÖM's measurements that the influence of this cause must depend in some unknown way on the density of the gas.

§ 17. Thus far, we have constantly assumed in our calculations that the coefficient η is very much larger than unity; this hypothesis has been confirmed by the values given in § 12 and, to judge from these numbers, it would even seem hardly probable that η can in any case have a value equal to, or smaller than 1. Yet, there is a phenomenon which can only be explained by ascribing to η a small value. This is the dissymmetry of the ZEEMAN effect, which has been predicted by VOIGT's theory²⁾ and has shown itself in some experiments of ZEEMAN³⁾. In so far as we are here concerned with it, it consists in a small inequality, observable only in weak magnetic fields, of the distances at which the two outer components of the triplet are situated from the place of the original spectral line. Whereas in strong fields the position of these components is determined by the equations $\xi = +\zeta$ and $\xi = -\zeta$, it corresponds to $\xi = 0$ and $\xi = 1$, if the magnetic intensity is very small.

VOIGT has immediately pointed out that the dissymmetry can only exist, if η is not very large. Yet, from the fact that the effect could scarcely be detected by ZEEMAN, he concludes that the coefficient must

¹⁾ ÅNGSTRÖM, Über die Abhängigkeit der Absorption der Gase, besonders der Kohlensäure, von der Dichte, Ann. Phys., 6 (1901), p. 163.

²⁾ VOIGT, Über eine Dissymmetrie der ZEEMAN'schen normalen Triplets, Ann. Phys., 1 (1900), p. 376.

³⁾ ZEEMAN, Some observations concerning an asymmetrical change of the spectral lines of iron, radiating in a magnetic field. These Proceedings, II (1900), p. 298.

have been rather larger than unity. In my opinion, we must go farther than that and ascribe to η a value, not sensibly above 1, my argument being that the dissymmetry can only make itself felt, if the difference between the distances from the original line to the two components in question is not very much smaller than the breadth of the line.

We know already (§ 9) that $\xi = 0$ at the middle of the line and $\xi = \eta$ at the border. Now, if η were sensibly larger than 1, the places corresponding to $\xi = 0$ and $\xi = 1$, i. e. the places occupied by the two components in a weak field, would lie within the breadth of the original line; it would therefore be impossible to discern the want of symmetry.

§ 18. Whatever be the exact value of η , ZEMAN'S experiments on this point show at all events that under favourable circumstances a displacement of a line, corresponding to a change from $\xi = 0$ to $\xi = 1$, or to a change

$$\frac{1}{2m'n_0} \dots \dots \dots (38)$$

of the frequency, is large enough to be seen. But, if such is the case, we shall no longer be right, if we discuss the value of ξ , in omitting quantities that are but a few times smaller than unity.

A quantity of this kind is the term α in the equation (11), which as has already been mentioned, is but little different from $1/2$, and which we have omitted in all our calculations. If we wish to take it into account, we shall find that all that precedes will still hold, provided only we replace n_0 by the quantity n'_0 , determined by

$$f'' - \alpha = m' n'_0{}^2 \dots \dots \dots (39)$$

Indeed, (28) may then be written in the form

$$\xi = m' (n'_0{}^2 - n^2),$$

and the place of maximum absorption, the middle of the line, will correspond to the frequency n_0 , exactly as it formerly corresponded to the frequency n'_0 .

Now, by (7) and (10)

$$f'' = m' n_0{}^2,$$

and by (39)

$$n'_0{}^2 = n_0{}^2 - \frac{\alpha}{m'}, \quad n'_0 = n_0 - \frac{\alpha}{2n_0 m'} \dots \dots \dots (40)$$

or, on account of (10),

$$n'_0 = n_0 - \frac{\alpha N e^2}{2 n_0 m} \dots \dots \dots (41)$$

We learn from this equation that an increase of the density must

give rise to a small displacement of the absorption line towards the side of the larger wave-lengths. A shift of this kind has been observed by HUMPHREYS and MOHLER in their investigation of the influence of pressure on the position of spectral lines. However, as the formula (41) does not lead to the laws the two physicists have established for the new phenomenon, I do not pretend to have given an explanation of it.

Nevertheless we may be sure that in those cases in which the dissymmetry of the ZEEMAN effect can be detected, the last term in (41), which in fact is of the same order of magnitude as the expression (38), can have an influence on the position of a spectral line that is not wholly to be neglected.

On the other hand, it now becomes clear that, in the case of a large value of η , the term α in (11) may certainly be neglected, its influence on the position of the middle of the line being much smaller than the breadth.¹⁾

§ 19. We shall conclude by examining the influence of the last term in (19), which we have likewise omitted. If we replace f by $f + \frac{m}{\tau^2}$ and, in virtue of (10), f' by $f' + \frac{m'}{\tau^2}$, which I shall denote by (f') , and if this time we neglect the term α , the formula (11) may again be written in the form (28). Indeed, if we put

$$n''_0 = \frac{(f'')}{m'} = n_0 + \frac{1}{\tau^2}, \quad (42)$$

we shall have

$$\xi = m' (n''_0 - n).$$

Instead of (42) we may write

$$n''_0 = n_0 + \frac{1}{2 n_0 \tau^2}, \quad (43)$$

an equation which shows that the absorption band lies somewhat more towards the side of the smaller wave-lengths than would correspond to the frequency n_0 and that its position would be shifted a little, if the time τ were altered in one way or another (§ 16). These displa-

¹⁾ Prof. JULIUS has called my attention to the fact that in many cases the absorption lines are considerably broadened by the change in the course of the rays that can be produced in a non-homogeneous medium by anomalous dispersion. In the experiments of HALLO, I have discussed, this phenomenon seems to have had no influence. This may be inferred from the circumstance that the emission lines of his flame had about the same breadth as the absorption lines.

cements would however be much smaller than half the breadth of the band. This is easily seen, if we divide the value of $n''_0 - n_0$ calculated from (43) by the value of $n - n_0$ that is given by (29). The result

$$\frac{1}{2 \nu n_0 \tau}$$

is (cf. § 12) a small fraction, because $n_0 \tau$ is equal to the number of vibrations during the time τ , multiplied by 2π .

(January 25, 1906).

KONINKLIJKE AKADEMIE VAN WETENSCHAPPEN
TE AMSTERDAM.

PROCEEDINGS OF THE MEETING
of Saturday January 27, 1906.

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(Communicated in the meeting of November 25, 1905).

Some time ago a paper was published by GOSSNER ¹⁾ on the crystal-forms of *Chlorobromonitrophenol*, *Dibromonitrophenol* and *Iodobromonitrophenol* being an experimental contribution to the knowledge of

¹⁾ B. GOSSNER, Krystallographische Untersuchung organischer Halogenverbindungen. Ein Beitrag zur Kenntniss der Isomorphie von Cl, Br und J. Zeitschr. f. Krystall. Bd. 40. (1905). 78—85.

the isomorphous substitution of the halogens *Cl*, *Br* and *I* in organic molecules. The author first gives a short résumé of the chief series of inorganic compounds where *Cl*-, *Br*- and *I*-compounds have been compared in regard to their crystal-form. Even in cases where a direct analogy in form does *not* occur an isodimorphism may be always proved to exist.

The *I*-compounds differ in most cases from the others as regards their behaviour.

Only a few complete series of analogous halogen derivatives of organic compounds have been investigated and in no case as to their mutual behaviour in the liquid state.

A complete crystallographical investigation was made of: *p*-Chloro-, *p*-Bromo- and *p*-Iodoacetanilide ¹⁾, the melting points of which are respectively, 179°, 167½° and 181°. The *Bromo*- and the *Iodo*-compounds are both *monoclinic*, the *Chloro*-compound differs and is *rhombic*. The *Br*- and the *I*-compound present in symmetry and parameters a distinct analogy with the *rhombic Cl*-compound; the plane of cleavage is, however, a totally different one ²⁾.

Cl-compound: Rhombo-pyramidal.

$a : b : c = 1,3347 : 1 : 0,6857$; $\beta = 90^{\circ}0'$. Cleavable towards {100}.

Br-compound: monoclinoprismatic. ³⁾

$a : b : c = 1,3895 : 1 : 0,7221$; $\beta = 90^{\circ}19'$. Cleavable towards {301}.

I-compound: monoclinoprismatic. ⁴⁾

$a : b : c = 1,4185 : 1 : 0,7415$; $\beta = 90^{\circ}29'$. Cleavable towards {301}.

Gossner ⁵⁾ proved that the *Cl*-compound is *dimorphous* and also that it possesses a *more labile monoclinic* form. On the other hand, the *Br*- and *I*-compounds are certainly also *dimorphous* but here the *rhombic* modification is the *more labile*. The more labile and the more stable modifications possess very analogous parameters, although their molecular structures are different. He thinks however that the *irregular positions of the melting points* may be satisfactorily explained from all this.

On the other hand, in the series *Chlorobromo*-, *Dibromo*- and *Iodobromonitrophenol*, all three derivatives are directly-isomorphous with each other. (Structure: $(OH) : (NO_2) : Br = 1 : 2 : 4$; *Cl*, *Br* and *I* on 6).

¹⁾ B. GOSSNER, Z. f. Kryst. **38**. 156—158. (1904).

²⁾ FELS, Z. f. Kryst. **32**. 386 (1900); Idem **32**. 406.

³⁾ MÜGGE, Z. f. Kryst. **4**. 385; FELS, Z. f. Kryst. **37**. (1903). 469; WILSON, Z. f. Kryst. **36**. 86. Abstract; PANEBIANCO, Z. f. Kryst. **4**. 393.

⁴⁾ SANSONI, Z. f. Kryst. **18**. 102.

⁵⁾ GOSSNER, Z. f. Kryst. **38**. 156—158.

This is the first properly investigated series of halogen-substitution products in organic chemistry where *Cl*, *Br*, and *I* replace each other in a directly isomorphous manner.

Notwithstanding this complete isomorphism there occurs here a remarkable abnormality in the position of the melting points, just as in the case of the isodimorphous *p*-Halogen acetanilides. This abnormality *cannot*, therefore, be explained in the manner described above; in fact it is quite incomprehensible:

<i>Cl</i> -compound:	m. p. 112° C.	Spec. gr.	2,111	Mol. Vol.	118,7
<i>Br</i> -	„ m. p. 117½° C.	„ „	2,434	„ „	121,1
<i>I</i> -	„ m. p. 104° C.	„ „	2,645	„ „	129,03

In this case it is the *I*-compound which exhibits an abnormal melting point.

From all this it is evident that there is still something strange, as regards the mutual morphotropic relations of the halogens, at least, in the case of organic compounds. Some facts relating thereto will therefore be communicated in what follows.

I have, frequently, published papers on the *Methyl esters* of *p*-Chloro-, and *p*-Bromobenzoic acid¹⁾. The *Chloro*- and *Bromo*-derivative each appeared to possess a different form, whereas the melting point line of binary mixtures should lead to the conclusion that an isodimorphism was present here, with a melting point line of the rising type, although it seemed impossible then to define by physico-chemical methods the *limits* of mixing for the two kinds of mixed crystals.

In order to treat the existing problem as fully as possible, I prepared first of all the corresponding *Fluoro*- and *Iodo*-compound.

p-Fluorotoluene kindly presented to me by Prof. HOLLEMAN was oxidised with KMnO_4 in alkaline solution, the *p*-Fluorobenzoic acid was separated with HCl and then esterified by means of methyl alcohol and hydrogen chloride. The ester, which has a strong odour of aniseed oil, is a liquid rendering measurements impossible, but on the other hand the acid could be measured crystallographically.

p-Toluidine was diazotised and converted by means of KI into *p*-Iodotoluene, this was distilled with steam, recrystallised and oxidised as directed to *p*-Jodobenzoic acid. In the same manner, *p*-Aminobenzoic acid was converted by diazotation etc. into its acid and this was

¹⁾ JAEGER, Neues Jahrb. f. Miner. Geol. und Palaeont. (1903). Beil. Bd. 1—28; Zeits. f. Kryst. 38. (1903). 279—301.

purified by sublimation. Both *Iodobenzoic acids* thus obtained were then esterified by means of methyl alcohol and HCl.

The product so obtained was purified by repeated recrystallisation from boiling alcohol until the melting point became constant at 114° .

The methyl ester of *p-Iodobenzoic acid* m.p. 114° crystallises from ether + alcohol in colourless needles, having a faint odour of aniseseed oil, which are very neatly formed, and exhibit the form of fig. 8.

Rhombo-bipyramidal.

$$a : b : c = 1,4144 : 1 : 0,8187.$$

Forms observed; $a = \{100\}$, predominant, very strongly lustrous, sometimes with delicate, vertical stripes; $p = \{210\}$, very sharply reflecting; $b = \{110\}$, narrow, often absent, but yields very sharp reflexes; $v = \{122\}$ and $r = \{011\}$, well-developed; $o = \{112\}$, very small and often absent altogether.

Habit: flattened towards $\{100\}$, with tendency parallel to the c -axis.

Angular measurements:

	<i>Measured:</i>	<i>Calculated:</i>
$a : p = (100) : (210) =$	$35^{\circ}15' \frac{1}{2}$	—
$b : v = (010) : (122) =$	$51^{\circ}49'$	—
$b : p = (010) : (210) =$	$54^{\circ}44' \frac{1}{2}$	
$v : v = (122) : (\bar{1}22) =$	$76^{\circ}23'$	$76^{\circ}22'$
$b : r = (010) : (011) =$	$50^{\circ}24' \frac{1}{2}$	$50^{\circ}41' \frac{1}{2}$
$a : v = (100) : (122) =$	$77^{\circ}29'$	$77^{\circ}23'$
$v : v = (122) : (\bar{1}22) =$	$25^{\circ}42'$	$25^{\circ}41'$
$r : r = (011) : (0\bar{1}1) =$	$79^{\circ}12'$	$79^{\circ}11'$
$v : r = (122) : (011) =$	$12^{\circ}50' \frac{1}{2}$	$12^{\circ}37'$
$p : r = (210) : (011) =$	$68^{\circ}23'$	$68^{\circ}33'$
$v : o = (122) : (112) =$	$17^{\circ}0' \frac{1}{2}$	$16^{\circ}43' \frac{1}{2}$
$o : o = (112) : (1\bar{1}2) =$	$43^{\circ}3'$	$42^{\circ}55' \frac{1}{2}$

Cleavable towards $\{010\}$.

The optical axial plane is $\{001\}$ with the b -axis as first bisectrix. The apparent axial angle in α -monobromonaphthalene is about 80° ; the dispersion is $\rho < v$. On a , p and b orientated extinction.

The sp. gr. of the crystals is: 2,020 at 10° ; the equivalent volume = 129,7.

Topic axes $\chi : \psi : \omega = 6,8179 : 4,8203 : 3,9464$.

From the above it follows that the *I*-compound is *perfectly isomorphous* with the analogous *Br*-compound. By way of comparison

some of the chief data observed in both compounds are placed here in juxtaposition:

<i>p</i> -Iodobenzoic Ester:	<i>p</i> -Bromobenzoic Ester:
Rhombo-bipyramidal	Rhombo-bipyramidal
$a : b : c = 1,4144 : 1 : 0,8187$	$a : b : c = 1,3967 : 1 : 0,8402$
Forms :	Forms :
{100}, {010}, {011}, {210}, {112}, {122}.	{100}, {010}, {011}, {210}, {112}, {122}
On {100} delicate stripes parallel <i>c</i> -axis.	On {100} delicate stripes parallel <i>c</i> -axis.
Cleavable along <i>b</i> .	Imperfectly cleavable along <i>b</i> .
Axial plane is {001}; 1 st Diag. is <i>b</i> .	Axial plane is {010}; 1 st Diag. is <i>b</i> .
Angles:	Angles:
$a : p = 35^{\circ}16'$	$a : p = 34^{\circ}56'$
$b : v = 51^{\circ}49'$	$b : v = 51^{\circ}10'$
$o : o = 42^{\circ}55$ etc.	$o : o = 43^{\circ}50'$ etc.

The dispersion in the *I*-derivative is of an opposite character to that in the *Br*-compound; the apparent axial angles are almost equal if that of the *I*-derivative is measured in α -Bromonaphthalene and that of the *Br*-derivative in oil of Cassia.

It seems remarkable, that in our case the *Bromo*- and *Iodo*-compounds behave in an analogous manner and that it is the *Chloro*-compound which exhibits here a *deviating* character.

In order to show the further relation of the three compounds the binary melting point lines were determined and represented in fig. 9.

The melting point line *Br-I*-compound does not deviate markedly from the straight line, the difference is really negligible. The lowering of the melting point of the *I*-derivate is, therefore, practically directly proportional to the number of added molecules of the *Br*-compound.

The melting point lines *Cl-I*- and *Cl-Br*-compound take an analogous course, that is to say, all the melting points lie between the lowest and the highest melting point. Both melting point lines belong to the *rising* type of ROOZEBOOM, which may occur in isodimorphous substances. The lower branch and the mixing limits could not be found by thermometrical methods. The existence of these two branches may indeed be proved, and they are even situated at some considerable distance from the top branches — at least at the side of the compounds having the highest melting points — as was found by Dr. B. R. DE BRUYN. It is, however, not possible to determine this line with sufficient accuracy. The progressive change of the cooling-curve is of such a nature that a discontinuity is observed from which we

may draw the above mentioned conclusion that the lower branch of the melting point line — at least at the side of the *rhombic* mixed crystals — is situated at a fairly considerable distance from the upper

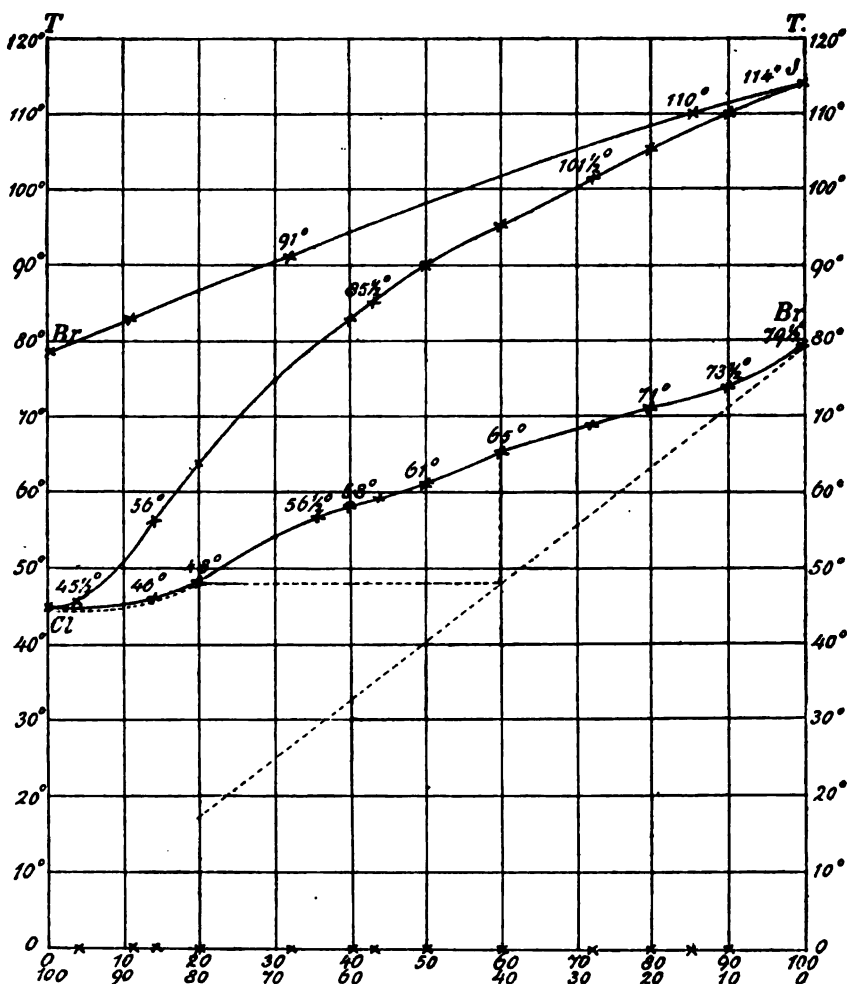


Fig. 9. Binary melting point lines of the three halogenised benzoic methyl esters.

branch. This change in direction of the cooling line is, however, so slight, that the true situation of the point on the lower branch cannot be indicated with certainty.

The determination of the mixing limits by an investigation of the solid phases, which are in equilibrium with solutions of known content, met with difficulties of an analytical character. An effort was, therefore, made to determine those mixing limits by the crystallographic process. For that purpose solutions were prepared of mixtures of the two esters, for instance of the *chloro*- and the *bromo*-ester,

in ether + alcohol, and the homogeneous mixed crystals obtained on slow evaporation were individually investigated crystallographically and then their melting point was taken, namely the temperature at which the last particle of solid matter disappears in the surrounding fused mass. If one may assume that this last solid particle, in each of the cases investigated, is really in *stable* equilibrium in regard to the fused mass, the temperature thus found, by comparison with the already found upper branch, indicates the molecule-percentage composition of the mixed crystal under investigation.

If we take little of the *Br*-ester and much of the *Cl*-ester, we obtain from the alcoholic solution *monoclinic* mixed crystals which possess quite the form and angular values of monoclinic *Cl*-ester itself. Of such crystals the melting point never exceeded $46\frac{1}{2}^{\circ}$. If the proportion of the components is reversed mixed crystals of a rhombic form are deposited quite analogous to the *Br*-ester. These crystals gave melting points from $79\frac{1}{2}^{\circ}$ down to 47° ; but not lower.

Assuming that the melting point of the end terms of the monoclinic series does not differ practically from 47° , it then looks as if rhombic mixed phases may exist which, at 47° as transition temperature, attach themselves *immediately* to the monoclinic terms. I have found, however, that rhombic mixed crystals with various melting points kept together in a closed tube for four months become turbid and partially opaque with a rough surface as soon as their melting point falls *below* 65° . It is also remarkable that the rhombic mixed phases of this kind are more and more badly formed and curved-planed, and that they become more distorted, as if existing in a kind of enforced condition, when their composition begins to differ from that at 65° towards the monoclinic side. It seems to me that when accepting the above hypothesis, all rhombic mixed phases below 65° represent *metastable* conditions, which, in the solid state, are very slowly broken up, to be partly converted into monoclinic terms.

That is to say the melting figure takes schematically the form of fig. 9; the said metastable conditions are then points situated on the extended part of the lower branch to the right, which indicates the composition of the rhombic mixed crystals coexisting with the fused mass. The stable hiatus in the mixing series then extends from 18% to 60% of the *Br*-compound.

From all this it follows that in consequence of the *very slow* conversion of the mixed crystals, no sharp determination of the mixing limits can be made in this manner when less than 60% *Br*-ester of monoclinic character is present.

In the system *Cl*-ester + *I*-ester the matter is still more troublesome.

There, the end term of the monoclinic mixing series is situated still much closer to the axis than in the case mentioned. In consequence of the very great difference in solubility of the *Cl*-, and the *I*-compound we never obtain here from alcoholic solutions anything else but *rhombic* very delicate needles, while the monoclinic phases crystallise so indistinctly that they are quite unsuitable for a serious investigation.

The *Br*-, and the *I*-ester readily crystallise together in *all* proportions with angular values which differ but little from those of the components. No optical anomalies could be found in such mixed phases. From this it follows that to those two halogen substitution products belongs an analogous molecular structure. Their molecular volumes in the solid condition agree indeed very well; the difference is smaller than between that of the *Cl*-, and *Br*-compounds.

As regards the lowering of the melting point of the compound melting at the higher temperature by addition of the one melting at the lower temperature, this is not proportionate to the number of added molecules, as in the system *Br*- + *I*-compound. In the mixtures of *Cl*- and *J*-ester, the observed values are always situated on a curve which occurs *above* the line of the proportionate lowering of the melting point; in the system *Cl*- and *Br*-ester, on a two-periodic curve which occurs *below* the said straight line.

It must also be observed that the mixed phases deposited from alcoholic solutions possess a larger content in the compound melting at the higher temperature than the solution from which they have formed. For instance, from a solution containing 20 % of *Br*-ester and 80 % of *Cl*-ester, mixed (*rhombic*) crystals were at first deposited which melted at 57° corresponding with a considerably higher percentage of the *Br*-compound.

The *Chloro*-compound which is *monoclinic* with:

$$a : b : c = 1,8626 : 1 : 3,4260, \text{ and } \beta = 64^{\circ}18'$$

and the forms:

$a = \{100\}$, $c = \{001\}$, $r = \{\bar{1}02\}$, $p = \{210\}$, $t = \{011\}$, $o = \{\bar{1}11\}$, $x = \{111\}$, $w = \{\bar{1}13\}$. presents a habit which is not at all like that of the two other derivatives, although that habit, as shown in fig. 1—5, is in a high degree variable, according to the choice of the solvent and temperature of crystallisation.

The habit of the *Br*- and *I*-compound is on the other hand perfectly analogous; in the *I*-ester it is, moreover, very constant under different conditions of crystallisation (fig. 8) whilst it is still some-

what changeable in the *Br*-ester (fig. 6 and 7), although no longer so strong as in the *Cl*-derivative. With an increasing atomic weight of the halogens, the changeability of the crystal-habit, owing to a change in conditions of crystallisation, decreases considerably and gradually.

The sp. gr. of the three compounds, their equivalent volume and their topic parameters are :

Cl-ester: $d_{40} = 1,382$; $V = 123,37$. $\chi : \psi : \omega = 5,1731 : 2,7774 : 9,5153$.

Br-ester: $d_{40} = 1,689$; $V = 127,29$. $\chi : \psi : \omega = 6,6611 : 4,7691 : 4,0070$.

I-ester: $d_{40} = 2,020$; $V = 129,70$. $\chi : \psi : \omega = 6,8179 : 4,8203 : 3,9464$.

It must be remarked here that the melting points of the three esters increase *regularly* by $35\frac{1}{2}^{\circ}$ notwithstanding the difference in crystalform : $44^{\circ} - 79\frac{1}{2}^{\circ} - 114^{\circ}$.

The above admits of no other explanation than the assumption that all three halogenised esters are dimorphous. The *Cl*-ester must still exist in a *more labile rhombic* form, and the *Br*- and *I*-esters in a *more labile monoclinic* form. In one of BRUNI's communications¹⁾ a "monoclinic" *p*-Bromobenzoic Methyl Ester is described by an Italian investigator with the object of proving an "isomorphism" with the analogous *p*-Nitrobenzoic ester. The given measurements have, however, absolutely no connection with those applied to the *p*-Chlorobenzoate, so that this monoclinic form can in no case be the one intended. Moreover, none of the measured angular values of the *p*-Bromo-derivative agree with those obtained by myself. It appears to me doubtful whether the measurements mentioned in BRUNI's paper are really correct or it may be that the operator has really not been working with *p*-Bromobenzoic Methyl ester at all. All efforts made by me to obtain from this substance a crystal form different to the *rhombic one* proved fruitless, whilst in the Italian treatise, the supposed "monoclinic" form is represented as a perfectly stable one which, therefore, occurs continuously.

In order to prove an eventually existing dimorphism of these substances, I have made use of LEHMANN's microscopical method with the aid of the crystallisation microscope constructed by him. It appeared, however, that in none of these cases a positive result could be obtained. I think that in the case of each of these substances, I can notice two different ways of crystallisation under the microscope, namely long, rather delicate needles and also parallelogram-limited

¹⁾ BRUNI and PADOA, Gazz. Chimic. Ital. (1904). 34a. 133—143; Rendic. Lincei (1903). 5a. 12. 348.

flat needles which exhibit higher interference colours and like the first named extinguish normally on the longitudinal direction. However, the difference — if present at all — is so indistinct that taking into consideration the inclination of these substances to alter their crystal-habitus under various circumstances in so high a degree, I dare not conclude to an already proved dimorphism. Experiments with mixtures richer or poorer in *Chloro-ester* also exhibited the same properties. It is, therefore, quite possible that we have two forms for each of the three substances, but this has not yet been *proved* and also it could not be ascertained whether in the given circumstances both eventually present forms stood to each other in the position of monotropy or enantiotropy.

A few short data as to the halogenised benzoic acids deserve mention.

1. *p-Chlorobenzoic acid* m.p. 243° has been measured by FELS (Zeitschr. f. Kryst. **32**, (1900) 389). It is monoclinic-prismatic, with $a : b : c = 1,2738 : 1 : 3,3397$, and $\beta = 78^{\circ}24\frac{1}{2}'$. The forms observed have intricate symbols; besides $a = \{100\}$ and $c = \{001\}$, he finds $d = \{\bar{2}07\}$, $o = \{111\}$, $e = \{233\}$, $u = \{\bar{3}22\}$, $v = \{\bar{4}11\}$. Sp.gr. = 1,541.

2. *p-Fluorobenzoic acid* m.p. 182° synthesised by me is also monoclinic-prismatic. If to the forms occurring here we assign the symbols: $a = \{100\}$, $c = \{001\}$, $r = \{\bar{2}03\}$, $s = \{\bar{4}03\}$, and $q = \{043\}$, the indices being therefore analogous to those given above, the parameters become:

$$a : b : c = 1,1917 : 1 : 3,1825$$

$$\beta = 78^{\circ}16'.$$

Although there exists here an undeniable difference in habit, I think I may still conclude that there is a direct isomorphism of the *Chloro-* and *Fluoro-*compound. A distinct plane of cleavage was not found. The melting point of *p-Fluorobenzoic acid* is also elevated by addition of the *Cl*-compound.

Angular values:

$$\begin{aligned} c' : r &= 69^{\circ}56' \\ r : s &= 15^{\circ}36' \\ s : a &= 16^{\circ}14' \\ c : a &= 78^{\circ}16' \\ c : q &= 76^{\circ}28' \\ q_1 : q_1 &= 27^{\circ}4' \end{aligned}$$

The habit is thin-tabled towards c , with a rectangular circumference. The crystals were obtained from alcohol + ether and were generally badly formed. The extinction on c is orientated.

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3. *p*-Bromobenzoic acid, m.p. 252° was obtained by me in tiny crystals from ethyl acetate + benzene but they were very badly formed. They are monoclinic and probably quite isomorphous with the two other acids. The angle of inclination amounts to about $78\frac{1}{2}^{\circ}$.

4. *p*-Iodobenzoic acid has not as yet been obtained in measurable crystals owing to its little solubility in most of the organic solvents. Its melting point is situated at 267° , therefore higher than that of the *Br*-derivative. A direct isomorphism with the three other halogen benzoic acids is not improbable.

Physiology. — “*On catalases of the blood*”. By L. VAN ITALLIE.
(Communicated by Prof. C. A. PEKELHARING.)

(Communicated in the meeting of December 30, 1905).

The discovery made by THÉNARD that bloodfibrine possesses the property of decomposing hydrogenperoxide has also been extended to defibrinated blood, by SCHÖNBEIN (*Journ. f. prakt. Chemie* **89**, 22). It has found a practical application in the judicial investigation on bloodtraces and has been the object of manifold scientific investigations. A resuming report precedes the investigations by SENTER (*Das Wasserstoffsuperoxyd zersetzende Enzym des Blutes. Zeitschr. f. physik. Chemie* **44** [1903] 257—318) to whose work we refer the reader. SENTER calls the enzyme which he has isolated from blood *Haemase* whereas I myself prefer to use the name of *catalase*, which has been given by LOEW (*Catalase, A new enzyme of general occurrence, Report N°. 68 U. S. Depart. of Agriculture. Washington*).

Although the catalases, those enzymes which are able to split H_2O_2 in water and oxygen, are universally scattered in the vegetable and animal kingdom, it has as yet not been possible to isolate one of these bodies in state of purity.

Although different phenomena indicate that there exist more than one catalase (apart from LOEW's α - and β -varieties) it has been impossible as yet to discern them.

The following communication gives a new contribution to the properties of the catalases of the blood, which may perhaps lead to a differentiation of the catalases, and which at least gives an opportunity of dividing the catalases of some animals into two groups.

To Mr. C. J. KONING at Bussum I owe the communication that human-blood diluted from 1—1000 heated at 63° for half an hour,

still contains a quantity of catalase whereas ox-blood under the same conditions no longer contains any catalase after half an hour. Want of time prevented the above mentioned gentleman from penetrating any further in this matter, so that he left the treatment of this subject to me.

The loss of activity of the catalase of the blood by heating has been investigated for ox-blood by SENTER (*l. c. p.* 293). Those investigations show that a diluted bloodsolution loses its activity in a quarter of an hour at 65°, that the rapidity of decomposition is considerably smaller at 55° and that the solution after having been heated for three hours at 45° still contains 60 % of the catalytic power, which it possessed originally.

Moreover it appeared that the loss of activity is not proportional to the present quantity of the enzyme, but that this phenomenon takes place with constant rapidity. I thought it useful to investigate the observed phenomenon with regard to some species of blood¹⁾ more closely and to see at the same time if it was possible to render the catalasereaction serviceable to the distinguishing of different species of blood.

Method of investigation. 5 cM³ of the different species of blood in a dilution of 1—1000 are heated for half an hour at 63°, then cooled down to 15° and mixed with 3 cM³ of a hydrogenperoxide solution of 1%. The mixture is put into a fermentation tube, such as are used at the investigation of urine on glucose. If the mixture still contains catalase the developing of oxygen begins within a few minutes so that by the development of this gas it is indicated whether catalase of the blood is present or not.

Human- and monkey-blood (*Macacus cynomolgus*) investigated in this way appeared to contain still catalase after having been heated at 63° for half an hour, whereas the blood of horses, oxen, pigs, goats, sheep, rabbits, caviae, rats, hares, chickens, pigeons, fish (flounder) and frogs did not show any reaction after the described treatment with H₂O₂ and did not split off oxygen within 3 hours.

Now the blood of some of these animals contains only a small quantity of catalase, but in the liver this substance is present in greater quantity. According to BATTELLI and STERN (*Compt. rendus* 138 [1904], 923-924) 10 mG. blood of a frog produces after being mixed with H₂O₂ of 1%, 7.5 cM³ oxygen in 5 minutes, whereas

¹⁾ For the providing of species of blood I am indebted to Messrs. W. C. SCHIMMEL and M. G. DE BRUIN, of the veterinary school at Utrecht and to Dr. J. BÜTTIKOFER, director of the zoological gardens at Rotterdam.

an equal quantity of the liver liberates 295 cM.³ oxygen in the same time.

The liver of a frog was mixed with purified sand, and the mixture thus obtained was shaken with water. A drop of the decanted liquid called about in a H_2O_2 -solution a turbulent development of O . If 5 cM.³ of the liquid was heated for half an hour it lost the power of decomposing H_2O_2 , quite, so that also with a considerable original catalytic power the above mentioned time is sufficient to make that power disappear.

In order to get an insight into the rapidity with which the catalase of the blood loses its activity I put into practice the following method of investigation for some species of blood.

5 cM.³ of the bloodsolution (1—1000) were put in some test-tubes; the tubes and their contents were heated for some time varying from 0—110 minutes in the thermostate at 63° , then cooled down to 15° and mixed with 10 or 20 cM.³ of a H_2O_2 -solution of 1%. The action having taken place, for $1\frac{1}{2}$ hour at 15° , the catalase-action was interrupted by adding 10 cM.³ diluted sulphuric acid and the quantity of hydrogenperoxide, which had not been decomposed was immediately titrated back with $\frac{1}{10}$ N. Kaliumpermanganatic solution. While the not heated bloodsolution indicates the quantity of H_2O_2 , which is decomposed by 5 milligrams of the used blood-species, it could be investigated at an arbitrary point of time in how far the catalytic action had been weakened by the heating.

At the used degree of concentration an oxidation of the catalytic may originate by the H_2O_2 , (SETER *l.c.* 279) but I would not reject the advantages which are offered by larger concentration as it was not wanted to get in the first place absolute figures.

In the table mentioned below the results of my investigations are written down while the graphic representation gives a more ample survey.

It is peculiar that here as well as at the blood investigations of UHLENHUTH and those of NEISSER and SACHS (*Berl. klin. Wochenschr.* 1905 N°. 44) the bloodspecies of related animals (man and monkey) show a relation with regard to catalytic power concerning the absolute strength as well as the greater resistance against the increase of temperature.

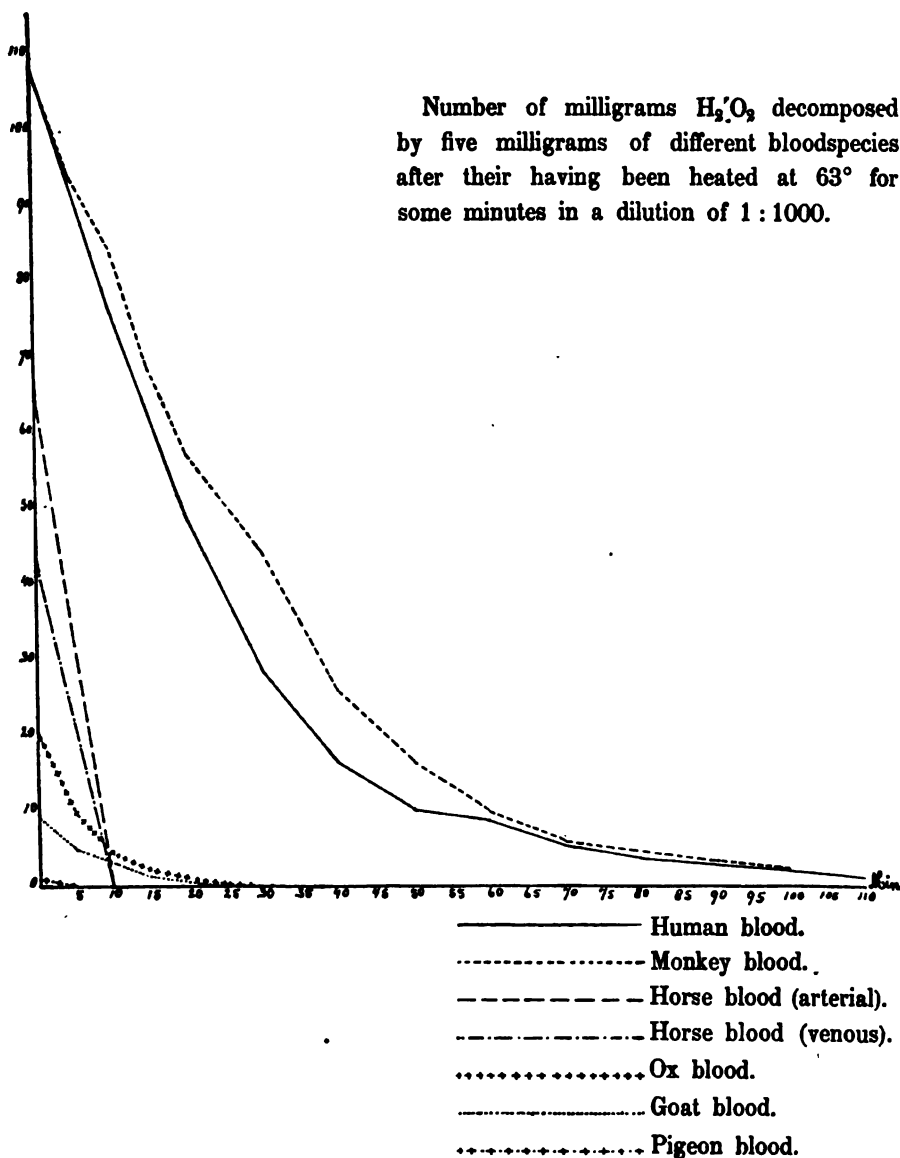
I think I may deduce from these investigations that the catalases occurring in the blood of different species of animals are not identical. My own observations, it is true extend to some individuals of the different species of animals only, but from reports of BATELLI and

Action of diluted bloodsolutions (1—1000) on hydrogenperoxide solutions (containing 1 pct. H_2O_2) after 5 cM². of the bloodsolution having been kept at 63° for the mentioned number of minutes and cooled down to 15°. Time of the influence of the H_2O_2 , one and a half hour at 15°.

Time of the heating at 63° in minutes.	Number of milligrams H ₂ O ₂ decomposed by						Developed quantity O in cM ² . (0° — 760 mm.							
	Human blood	Mon- key blood	Horse blood (arterial)	Horse blood (venous)	Ox blood	Goat blood	Pigeon blood	Human blood	Mon- key blood	Horse blood (arterial)	Horse blood (venous)	Ox blood	Goat blood	Pigeon blood
0	107.8	107.3	66.6	43.9	20.7	8.8	0.7	3.55	3.53	2.19	1.44	0.68	0.29	0.02
5		83.5			9.7	4.9	0		3.07			0.32	0.16	0
10	76.5	84.5	0	0	4.1	3.1	0	2.52	2.77	0	0	0.13	0.10	0
15		68.9			2.2	1.3			2.26			0.07	0.04	
20	48.3	57.6	0	0	1.2	0.5		1.58	1.89	0	0	0.04	0.016	
25		—			0.2	0			—			0.006	0	
30	28.9	44.4			0			0.95	1.45			0	0	
35		—												
40	16.8	26.2						0.55	0.86					
45														
50	10.2	16.7						0.33	0.55					
55														
60	8.7	10.0						0.29	0.33					
65														
70	5.4	6.3						0.18	0.20					
75														
80	3.9	—						0.13	—					
85														
90	3.0	3.6						0.10	0.12					
95														
100	2.2	2.9						0.07	0.095					
105														
110	1.4							0.046						

HALIFF (*Soc. biol.* 57 [1904] 264) it appeared already that the same organs of animals of the same species contain mostly about equal quantities of catalase and that this quantity is not dependent on the

mG. H_2O_2



temperature of the body nor on the metabolism. To illustrate the catalytic power of the bloodspecies which I investigated quantitatively I add a short survey,

Quantity of oxygen in cM.³ (0°—760 mm.) obtained from the action of 1 cM.³ blood on a solution of H₂ O₂ of 1%.

Man	710
Monkey	706
Horse (venous)	288
Horse (arterial)	438
Ox	136
Goat	58
Pigeon	4

Utrecht, December 1905.

Physiology. — *"On the differentiation of fluids of the body, containing proteid."* By L. VAN ITALLIE. (Communicated by Prof. C. A. PEKELHARING).

(Communicated in the meeting of December 30, 1905).

For the research of blood, sperm and other fluids of the body, containing proteid, the phenomenon, that even traces of these substances are able to decompose hydrogenperoxide, has been used for a long time already. If a drop of a hydrogenperoxide-solution is put on an object on which blood or sperm was dried up, development of gas is observed, even by the presence of traces of blood or sperm which give rise to the forming of froth, when blood is present. As the experiment can already be taken with some fibres, and the splitting off of oxygen can be traced under the microscope, it has often rendered me good services in examining on behalf of the court of justice, at the preliminary-examinations. If then no oxygen is liberated and the object on which dubious stains occur, has not been exposed to a temperature higher than 65°, it may be concluded from the fact that no reaction occurs, that blood and sperm were absent.

It was obvious to try to render the result of the experiments communicated in the preceding paper, serviceable to the distinguishing of the blood of men, resp. monkeys, from the blood of other species of animals. Not every one is in the possession of the serum of UHLENHUT or of the sera recommended by NEISSER and SACHS (Berl. klin. Wochenschr. 1905, number 44) for the anti-complementary influence, while it may be moreover of great value to the court of

justice to have within some hours the certainty whether bloodstains appearing on an object, originate from human blood (in our country of course monkey blood may as a rule be left unconsidered).

It is now indeed possible to show the presence of human blood (resp. of the monkey) in older stains with the aid of the catalase of the blood. I wish to draw the attention to this that the presence of blood must have been proved by a preceding microscopical, chemical or spectroscopical investigation because other fluids of the body too (sperm and milk) cause a reaction of catalase.

The method of investigation is simple. If the dubious blood trace is dried on some tissue, a piece of it is extracted with water at the ordinary temperature and the extract is divided into two parts. One part is mixed with a solution of hydrogenperoxide of 1%, and the mixture is put into a fermentation tube. The other part is heated for half an hour in a waterbath at 63°, then cooled down to 15° and after having been mixed with a solution of H_2O_2 , it is also put into a fermentation tube. If within some hours oxygen develops in both tubes, it may be concluded that human -- (resp. monkey-) blood is present; the quantity of oxygen in the second tube is of course smaller than that in the first. When active catalase of the blood is present the splitting off of oxygen begins soon after the mixing, and is finished in some hours.

If however only in the first tube oxygen is split off and the second tube does not show any development of gas, it follows that the catalase of the blood has become inactive by the heating to 63° for half an hour, and that the dubious blood does not originate from man or monkey.

I was in the opportunity of applying these experiments to fresh bloodstains of man, dog, ox and horse and to bloodstains on linen from the year 1903 originating from man, oxen, horses, goats and pigs. The old bloodstains gave the same results as the fresh blood.

If we dispose of more bloodstains we can follow the process of the reaction somewhat quantitatively by preparing for instance a larger quantity of extract with water, dividing this in parts of 5 cM.³, heating this to 63° during different periods in test-tubes and mixing it with H_2O_2 , and titrating it, as has been communicated in the preceding paper. The peculiar process of the reaction, graphically expressed, does not give a representation of the absolute quantity of the catalase of the blood which is present, but is so characteristic that human- (and monkey-) blood can be easily distinguished from that of another species of animal, even in the dried state.

It is hardly necessary to mention separately that the reaction of the catalase can be made serviceable to the distinguishing of mother's and cow's milk.

Cow's milk which has been heated to 63° for half an hour no longer possesses the property of decomposing H_2O_2 , a property which mother's milk still possesses in a rather considerable measure under the same circumstance.

In a mother's milk which I thank to the kind interference of Prof. KOUWER I found the following results, but it should be observed that the action of the milk on the solution of hydrogen-peroxide found place in the nitrometer of LUNGE and that I read off the volume of the developed oxygen after twelve hours :

5 cM. ³ mother's milk not heated gave	24.8 cM. ³ oxygen.
5 " " " heated to 63° for a	
quarter of an hour gave	18.5 " "
5 " " " " 3 " " " " "	7.5 " "
5 " " " " for an hour " "	4.0 " "

Utrecht, December 1905.

Physics. — “*Some remarks on the quantity H in BOLTZMANN's “Vorlesungen über Gastheorie”.*” By O. POSTMA. (Communicated by Prof. H. A. LORENTZ).

(Communicated in the meeting of December 30, 1905).

§ 1. It seems to me that some of the views advanced in one of the first paragraphs of the above mentioned work, are inaccurate; and it may be desirable to draw attention to this fact, because several considerations of BOLTZMANN and others are based on them. I mean § 6 on the “*Mathematische Bedeutung der Grösse H* ”.

In the case of a gas the molecules of which are all of the same type, this quantity is represented by $\int f \cdot l f \cdot d\omega$. Now, in § 5, assuming that the gas is of the simplest nature and that the motion of the molecules is “molecular-ungeordnet”, BOLTZMANN has shown that, in general, the quantity H decreases by the collisions and is minimum in the stationary state.

Such a gas would therefore move of its own accord to the stationary state i.e. with MAXWELL's distribution of velocities, as BOLTZMANN shows further on.

Now it is demonstrated in § 6 that the quantity H has also

another meaning, and that the circumstance that H is minimum implies that the probability of the corresponding distribution of velocities, indicated by the function f , is maximum. Afterwards the connection between H and the entropy is indicated in § 8 on the "Physikalische Bedeutung der Grösse H ".

The meaning of H in question being very incompletely derived in § 6, we shall have to consult Vol. 76 of the Sitzungsberichte der Wiener Akad., to which BOLTZMANN refers, and Vol. 72, to which he refers in Vol. 76.

In § 6 p. 40, BOLTZMANN begins with the following reasoning: "Für alle Zusammenstösse, für welche der Geschwindigkeitspunkt des einen der stossenden Moleküle vor dem Zusammenstosse in einem unendlich kleinen Volumelemente lag, befindet sich derselbe, wie wir sahen, bei Constanz aller anderen, den Zusammenstoss charakterisirenden Variabeln nach dem Stosse wieder in einem Volumelement von genau gleicher Grösse. Theilen wir daher den ganzen Raum in sehr viele (ξ) gleichgrosse Volumelemente ω (Zellen), so ist die Anwesenheit des Geschwindigkeitspunktes eines Moleküls in jedem solchen Volumelemente mit der Anwesenheit in jedem anderen Volumelemente als ein gleichmöglicher Fall zu betrachten, gerade so wie früher der Zug einer weissen oder einer schwarzen oder einer blauer Kugel."

So it is as if the velocities were assigned to the molecules by taking for every molecule a slip of paper from a box, which box would be filled with slips of paper each indicating a unit of volume of the "whole space". The probabilities a priori are therefore equal that the components of the velocity ξ, η, ζ lie between two values which differ $d\xi, d\eta, d\zeta$.

Here at least something has been adduced to account for the fact that these probabilities are equal, which has not been attempted in Vol. 76 of the W. S. We have to derive it from the fact, that at a collision the "points of velocity" skip from a certain volume into one of the same size (cf. the "daher" of the quotation). For me this has, however, by no means convincing force; for that one point always skips from a volume to one of the same size does not prove that it can just as well be found in *any* volume of the same size. We shall presently show that this can hardly be assumed.

But let us first proceed. Let us assume n molecules are to have a velocity, then the probability a priori that of them n_1 ω have their "point of velocity" in the first volume ω , n_2 ω in the second volume etc. is proportional to $Z = \frac{n!}{(n_1 \omega)! (n_2 \omega)! \dots}$, where $(n_1 + n_2 + \dots) \omega = n$.

If we now assume that for $p!$ may be taken $\sqrt{2p} \pi \left(\frac{p}{e}\right)^p$, we get $lZ = -\omega(n_1 l n_1 + n_2 l n_2 + \dots) + C$, and so Z is maximum when $\omega(n_1 l n_1 + n_2 l n_2 + \dots)$ is minimum or when $\int f(\xi \eta \zeta) l f(\xi \eta \zeta) d\xi d\eta d\zeta$ is minimum, or when H is minimum, if we have a simple gas.

The distribution of the velocities $f(\xi \eta \zeta)$ for which H is minimum, is therefore also that with the greatest probability, concludes BOLTZMANN. So the stationary state with MAXWELL's distribution of velocities is at the same time the most probable (p. 42).

This, however, follows by no means from the above, for the stationary state is that, for which the change of H with the time in consequence of the collisions $= 0$, whereas the most probable state here is that for which *every conceivable* variation of the numerator of $Z = 0$.

Not before the condition is taken into consideration that the kinetic energy of n molecules must have a definite value, as BOLTZMANN does in Vol. 76 and 72, it can appear whether the result is the same.

Now

$$H = \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} f(\xi \eta \zeta) l f(\xi \eta \zeta) d\xi d\eta d\zeta$$

must be minimum, while the conditions

$$n = \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} f(\xi \eta \zeta) d\xi d\eta d\zeta$$

and

$$L = \frac{m}{2} \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} (\xi^2 + \eta^2 + \zeta^2) f(\xi \eta \zeta) d\xi d\eta d\zeta$$

exist, when m is the mass of every molecule, and L the kinetic energy of n molecules.

In Vol. 72 p. 450 BOLTZMANN gives the solution of this, and it appears that when no external forces exist,

$$l f(\xi \eta \zeta) + \lambda + \mu \cdot \frac{1}{2} m (\xi^2 + \eta^2 + \zeta^2) = 0$$

where λ and μ are constants which are still to be determined.

From this follows MAXWELL's distribution of velocities.

But what probability problem has now been solved? I cannot see that any has been solved but the following: From a box with slips of paper, each indicating a volume element, one has been taken at

random for each of the n molecules of a certain quantity of gas; the "point of velocity" of the molecule was every time placed in the volume element extracted. The n velocities which have been extracted chanced to be such that the sum of the energies of the molecules has a definite value L . What distribution of the velocities among those n molecules is now a posteriori the most probable?

The most probable is therefore the distribution of MAXWELL. But this is a problem without importance for the gas theory. For it is easy to see that the mean velocity indicated by the slips of paper in the box is infinitely large, so that if from this n slips of paper are taken at random, in general the mean velocity, which is indicated by them, is also infinitely large, and there is only an infinitely small chance, that the energy of the n molecules becomes finite. If we now see that of every finite gas-mass the energy is finite, we cannot assume that the velocities would have been assigned to the molecules in the way mentioned above. The chances a priori for every velocity must, therefore, not be considered as equal.

The mean velocity in the box may be calculated as follows.

If in the unity of volume there are c points of velocity, then in a spherical shell with radius r and thickness dr there are: $4 \pi r^2 c dr$. The sum of the velocities now is $4 \pi r^3 c dr$, and so for a sphere with radius $r = \pi r^4 c$. The number of points of velocity in the sphere is $\frac{4}{3} \pi r^3 c$, so the mean velocity $= \frac{3}{4} r$.

For the whole space, therefore, the mean velocity is infinitely large. In this way it is proved that the hypothesis of the equality of the chances a priori is inaccurate, and so also the result that MAXWELL's distribution of velocities is the most probable state.

§ 2. Of course nothing is said here in derogation of the proof, that MAXWELL's law holds in the stationary state, which BOLTZMANN gives in the §§ preceding § 6 and in § 7. But it is incorrect to speak of transition of probable to improbable states when the meaning is from stationary to non-stationary states. This incorrect view gives rise to wrong considerations when BOLTZMANN discusses the fiction of the reversal of the molecular velocities in the last part of § 6.

It is assumed there, that a gas has originally a "molecular-ungeordnet" but "improbable" distribution e.g. all molecules have the same velocity. The gas moves now to the stationary state with MAXWELL's distribution of velocities. But before it is reached, all velocities are reversed, which causes the same conditions to be passed through but now in reversed succession. This will cause H to increase. Is

this not incompatible with § 5, where it is proved that $\frac{dH}{dt}$ can only be negative or zero? No, says BOLTZMAN, for the reversed motion is not one for which this theorem holds, because the motion is "molecular geordnet". For the molecules, which a molecule with a certain velocity meets, are not taken at haphazard from the whole number but their velocities are connected with that of the molecule under consideration. This is specially clear when at the moment of reversal the motion had not yet lasted long.

Now, however, BOLTZMANN meets with another difficulty, which is to be removed. Does the increase of H not also clash with the laws of probability, as the smallest H gives the most probable state?

No, for the increase of H is only improbable, not impossible.

This difficulty seems to me to have only been raised by the incorrect view discussed above. The smallest H is not the most probable. Moreover we do not do justice to the subjectivity of statements concerning probability, when we speak of a transition from probable to improbable states, as if objective properties of substances are expressed in this way. BOLTZMANN loses repeatedly sight of this; particularly at the end of the second part of his "Gastheorie".

In my opinion the views on this matter of Dr. A. PANNEKOEK, occurring in these Proceedings, Vol. VI, p. 42¹⁾ are not perfectly correct either.

The latter assumes also that in the above mentioned case of reversal the reversed motion is "molecular-geordnet", and tries now to make clear what this means. With perfect justice he says, that it does not mean, as seems to be sometimes assumed, that the state may be calculated beforehand; this might also be done in the original case if the initial state was known. Now, however, we get the im-

¹⁾ Another remark on this subject. Under 2 we read: "one more remark, however is to be added", on which something follows, that does not supplement what has been said, but is in direct opposition to it. Moreover, the author seems to confound the collisions in the fictitious system (after reversal of the motions) and what BOLTZMANN calls the collisions of the opposite kind.

For it is not correct that the points Q_1Q_1' , R_1R_1' return to P_1P_1' in the reversed system; by reversal of the velocity we get a point of velocity lying diametrically opposite to the first.

Also 3 gives rise to different questions. As e. g. is it altogether correct that in the statistical way of treatment the direction of the normal of collision is considered as independent of the velocities? It can certainly not be independent of the relative velocity? And further: does the fact, that in the calculations it is assumed that the molecules do not hinder each other when colliding against a third, give sufficient justification for calling the radius of a molecule small of the first order with respect to the distances of the molecules?

pression that Dr. PANNEKOEK considers as the distinctive feature which renders the original motion "ungeordnet" its dissipating influence, and that which makes us call the reversed motion "geordnet" its bringing the velocity points nearer together. When in consequence of the collisions the "points of velocity" get dissipated the state would be "ungeordnet", when they draw nearer to each other, it is "geordnet". But this holds only in this special case; and it might just as well be just the reverse.

For what does "molecular-ungeordnet" mean. This appears when we examine the place where BOLTZMANN introduces this idea. We find it p. 20 in the formula (17): $Z_\phi = \Phi F_1 d\omega_1$. Here Φ represents the sum of the contents of all the oblique cylindres, into which a molecule of the 2nd kind must get in order to collide with one of the 1st kind. The formula now expresses that the molecules of the 2nd are, in proportion to the volume, as numerous in all these cylindres together as in the whole gas mass, or that these cylindres constitute a quantity taken at random from the gas mass with regard to the molecules of the 2nd kind.

Now in my opinion an "ungeordnete" distribution might very well be imagined, in which the points of velocity are more dissipated than in the stationary state. And of a gas in such a state the points of velocity would be brought nearer together by the collisions till MAXWELL's distribution of velocity is reached.

§ 3. With reference to the foregoing Prof. LORENTZ was so kind as to direct my attention to the work of JEANS on the kinetic theory ¹⁾. In this work a derivation of MAXWELL's distribution of velocities occurs, which is called a new one by the author, but which essentially agrees with the reasoning of BOLTZMANN in the above mentioned § 6 on the "Mathematische Bedeutung der Grösse H ", though the outward form is quite different. It is true that an important improvement has been made, which for the first time renders it in reality a derivation of the law; it is viz. not only demonstrated there, that the most probable state of a gas is that, for which the distribution of velocities in question occurs, but also that the chance is very great that a state will make its appearance, differing but very little from the most probable: for when it is only known that a state is the most probable, its probability may yet be so very small, that it does not say anything as to whether that state will occur or not.

Accordingly JEANS calls this most probable state the "normal state", in which he is now perfectly justified.

¹⁾ "The dynamical Theory of Gases" by J. H. JEANS; Cambridge, 1904.

The "normal" state is now the same as the "stationary" state. However, the same objection applies to this derivation as to that of BOLTZMANN.

JEANS calls his method "The method of General Dynamics" in opposition to the usual one, with the aid of collisions, which he calls "The statistical Method". This name, however, does not seem very appropriate to me; the considerations here are just as much statistical as in the usual method. Dynamics do not play any part in it but this, that the state of a gas with N molecules, so determined by $6N$ -coordinates and components of velocity, is represented by a point in a $6N$ -dimensional space, and that now the change of state of the gas runs parallel with the motion of this point in the generalized space.

A great number of possible states gives therefore a great number of points, and their changes a great number of orbits, the general course of which is to be studied. Instead of with these mathematical points we may also imagine the generalized space to be filled with an homogeneous liquid, the motion of which we must examine, which then according to the author is a "steady-motion" in hydrodynamic sense, the stream-lines of which are determined by the property that their energy is constant.

This, however, brings us about to the end of the dynamic considerations. They form an illustration, but nothing is proved by them.

The author now examines, what part of the generalized space is taken up by points representing systems of a certain state. But this is the same as what BOLTZMANN calls the probability of a system of a certain state. Both represent the proportion of the number of systems of equal possibility possessing a certain property, to the total number of systems. The objections to be made to the expression for the probability hold also for that of the part of the space.

JEANS treats successively two problems:

1. What part of the generalized space is occupied by the systems with a certain distribution of the coordinates of the molecules (or what chance is there of a certain distribution of density of the gas) and in connection with this: how are the systems distributed in that space with regard to the distribution of the coordinates.

2. What part of the generalized space is occupied by the systems with a certain distribution of velocities of the molecules (or what chance is there of such a distribution) and how are the systems distributed in that space with regard to the distribution of velocities?

Only the first problem is fully treated by JEANS; for the second, the most important, we are referred to the first.

It is then assumed that the gas is inclosed in a vessel with capacity Ω , divided into n elements ω , so that $n\omega = \Omega$. We imagine now a certain distribution of density, at which a_1 molecules are placed in the first element of volume, a_2 in the second etc. The number of ways, in which N molecules may be distributed over the n elements, so that every time this distribution of density exists is

$\frac{N!}{a_1! a_2! \dots a_n!}$. For each of these ways every molecule must be placed in a certain element of volume from the n and so the

representative point" is restricted to the $\frac{1}{n}$ part of the whole generalized space, in the same way with the following, so "the representative points will occupy the fraction n^{-N} of the whole of the generalised space". This is in somewhat different words nothing but "the chance of each of the combinations is n^{-N} ", and the reasoning rests evidently on the assumption that *each molecule has every time an equal chance to any place in the vessel*.

The representative points of the systems with this distribution of velocities occupy therefore together a part of the generalized space

$= \frac{N!}{a_1! a_2! \dots a_n!} n^{-N}$ (which therefore represents the total chance; an expression agreeing perfectly with the chance of a certain distribution of densities in § 1). After a similar reduction as in BOLTZMANN follows

from this: the part of the generalized space (chance) $= \frac{n^{1/2N}}{(2\pi N)^{\frac{n-1}{2}}} e^{-NK_a}$,

where $K_a = \frac{1}{N} \sum_{s=1}^n \left(a_s + \frac{1}{2} \right) \log \frac{na_s}{N}$ in the above mentioned distribution (A). Now, neglecting $\frac{1}{2}$ by the side of a_s we may consider K_a as a special value of the general function:

$$K = \frac{1}{\Omega} \iiint \frac{v}{v_0} \log \frac{v}{v_0} dx dy dz,$$

integrated over the vessel, where v represents the molecular density as function of the coordinates of an arbitrary point, and v_0 the mean density throughout the vessel. K is a function corresponding closely with BOLTZMANN'S H , specially when we leave out the constants and write:

$$K = \iiint v \log v dx dy dz \text{ just as } H \text{ was } \iiint f \log f dx dy dz ;$$

v is the density function, just as f is the function of velocity.

K is now minimum when $a_1 = a_2 = \text{etc.}$ or when $v = \text{constant}$. It is obvious that this also means "the part of the generalized space", is maximum or the chance is maximum. So on the above assumption the most probable distribution is that of uniform density.

Now JEANS proves further, that also by far the greater part of the generalized space contains systems which differ infinitely little from these with minimum K , so that this state may be called the normal one. Expressed in the other way this is, that the chance is infinitely great of a state deviating infinitely little from the most probable state. Though JEANS' proof does not seem faultless to me (no sufficient attention is paid, in my opinion, to the order of magnitude of infinitesimals) yet the result seems to me to follow from BERNOULLI's theorem, provided "systems differing infinitely little" is taken in the proper sense.

So JEANS concludes: it is clear that the gas-masses with uniform density will represent the ordinary case.

The second problem might be treated in the same way. Instead of the molecules which are to be distributed over the elements of volume of the vessel, we have now the velocity points of the molecules which are to be distributed over the elements of volume of the whole space. We get now in the same way for the part of the generalized space occupied by systems with a certain distribution of velocities, the expression $\frac{N!}{a_1! a_2! \dots a_n} n^{-N}$, but now N is infinitely large. According to the other mode of expression this is again the chance to that distribution of velocities.

The treatment of the problem is further the same as that of the first, but now we have to do with the quantity H . And finally it may be proved, that by far the greater part of the generalized space is occupied by systems which differ very little from that with minimum H or the normal state is that for which H is about minimum, from which, taking into account the condition that the energy $= E$, MAXWELL's distribution of velocities follows.

Now it is, however, clear that the same objection may be raised to this reasoning as to that of BOLTZMANN.

The above expression for the part of the generalized space (or the chance) rests on the assumption that the representative points are distributed uniformly throughout the generalized space also here, or that for every molecule the chance that the point of velocity gets into a certain element of volume, is independent of the place of that element. What now does the condition, that the energy $= E$, mean? Either that attention has been paid to it in the distri-

bution of velocities or not. If no attention has been paid to it, it is not to be accepted that the energy always becomes finite (see § 1); if attention has been paid to it, the chance a priori can no longer be taken equal for each element of volume, and the above expression is faulty, and so also the further reasoning.

So it seems to me that also this derivation of JEANS must be considered as incorrect¹⁾.

Botany. — Some remarks on the work of Mr. A. A. PULLE, entitled: "*An enumeration of the vascular plants known from Surinam, together with their distribution and synonymy.*" By Prof. F. A. F. C. WENT.

Mr. PULLE has worked out the botanical material collected by the expeditions of the last years, of one of which he was a member himself. He has also tried to render our knowledge of the flora of Surinam more complete by incorporating into his work the older collections which are preserved at Leyden, Utrecht, Göttingen, Berlin, Kew Gardens and in the British Museum.

In this way a total number of 2100 vascular plants appeared to be known for Surinam and although it may be said with certainty that this number is far from representing the real number of species, occurring in our colony, yet we must appreciate that here for the first time a comprehensive idea is given of the flora of Surinam.

Without entering into further details it must be mentioned that the author is led to the important result that phytogeographically Surinam belongs to the Hylaea, the region of the Amazon river, with the exception perhaps of the still unknown territory west of the Wilhelmina range. The Hylaea would then extend from the mouth of the Amazon river over French Guyana and Surinam and gradually form a narrow littoral strip in British Guyana, finally passing into the Orinoco district. As a consequence of this the conception must be given up that across Surinam there is found a continuous savannah district, such as occurs in Demerara and more to the west; where savannahs are found in our colony their presence must be entirely attributed to local influence of the soil.

¹⁾ JEANS' derivation occurs for the first time in the Philos. Magazine VI, 5, 1903, under the title of "The Kinetic Theory of Gases developed from a New Standpoint" p. 597. That also the "molecular ungeordnet" hypothesis is implied, which JEANS denies, is proved by BURBURY in the same magazine VI, 6, 1903 in an article on "Mr. J. H. JEANS' Theory of Gases" p. 529.

Mathematics. — "*The quotient of two successive Bessel Functions*".
(2nd paper). By Prof. W. KAPTEYN.

In our preceding paper we gave the value of the general coefficient of the expansion

$$\frac{I^{v+1}(z)}{I^v(z)} = f_1 z + f_2 z^2 + f_3 z^3 + \dots$$

Now we wish to draw the attention to a couple of relations which exist between these coefficients. The first is obtained from a particular integral of the following differential equation of RICCATI

$$z \frac{du}{dz} + u^2 + 2v u + z^2 = 0. \quad (1)$$

Putting

$$u = -\frac{z^2}{2(v+1) + u_1}$$

this differential equation reduces to

$$z \frac{du_1}{dz} + u_1^2 + 2(v+1)u_1 + z^2 = 0.$$

Repeating this process, it is evident that the equation (1) is satisfied by the continued fraction

$$u = -\frac{z^2}{2(v+1)} - \frac{z^2}{2(v+2)} - \frac{z^2}{2(v+3)} - \text{etc.}$$

which represents the value of $-z \frac{I^{v+1}(z)}{I^v(z)}$.

Introducing therefore

$$u = -f_1 z^2 - f_2 z^4 - f_3 z^6 - \text{etc.}$$

in the equation (1) we have

$$2(v+1)f_1 = 1$$

$$2(v+n+1)f_{n+1} = f_1 f_n + f_2 f_{n-1} + \dots + f_n f_1 \quad (I)$$

where $n = 1, 2, 3, \dots$

The second relation may be deduced from our former equation

$$a_1^{n+1} a_2^n \dots a_n^2 a_{n+1} f_{n+1} = (-1)^n \begin{vmatrix} \lambda_1 & x_1 & \epsilon_1 & \theta_1 & \dots & \zeta_1 & \epsilon_1 \\ \lambda_2 & x_2 & \epsilon_2 & \theta_2 & \dots & \zeta_2 & \epsilon_2 \\ \dots & \dots & \dots & \dots & \dots & \dots & \dots \\ \lambda_{n-2} & x_{n-2} & \epsilon_{n-2} & \theta_{n-2} & \dots & 0 & 0 \\ \lambda_{n-1} & x_{n-1} & 0 & 0 & \dots & 0 & 0 \end{vmatrix}$$

where

$$a_p = 2(v + p),$$

$$\lambda_p = \frac{(2n - p - 1) \dots (2n - 2p)}{p!} a_{p+1} \dots a_{2n-p-1}$$

$$\kappa_p = \frac{(2n - p - 2) \dots (2n - 2p - 1)}{p!} a_{p+1} \dots a_{2n-p-2}$$

$$\dots \dots \dots$$

$$\varepsilon_p = \frac{(n - p + 1) \dots (n - 2p + 2)}{p!} a_{p+1} \dots a_{n-p+1}$$

and h stands for $\frac{n}{2} - 1$ when n is even or for $\frac{n-1}{2}$ when n is odd.

Putting $a_p = 2b_p$ this equation may be written

$$2^{2n+1} b_1^{n+1} b_2^n \dots b_n^2 b_{n+1} f_{n+1} = D_n \dots \dots \dots (2)$$

and it is found that the determinant D_n satisfies the condition

$$D_n = nb_1 \dots b_n D_{n-1} - \frac{n-1-n-2}{2!} b_1 \dots b_n \cdot b_1 \dots b_{n-1} D_{n-2} + \\ + \frac{n-2 \cdot n-3 \cdot n-4}{3!} b_1 \dots b_n \cdot b_1 \dots b_{n-1} \cdot b_1 \dots b_{n-2} D_{n-3} - \text{etc.}$$

the last term being

$$(-1)^{\frac{n}{2}-1} \left(\frac{n}{2} + 1 \right) b_1 \dots b_n \cdot b_1 \dots b_{n-1} \dots b_1 \dots b_{\frac{n}{2}+2} \cdot b_{\frac{n}{2}+1} \frac{D_n}{2}$$

when n is an even number, and

$$(-1)^{\frac{n-1}{2}} b_1 \dots b_n \cdot b_1 \dots b_{n-1} \dots b_1 \dots b_{\frac{n+3}{2}} \frac{D_{n-1}}{2}$$

when n is odd.

Substituting in this equation D_p by their values from (2) we get this second relation between the coefficients f_p

$$\leq \frac{n-1}{2} \\ f_{n+1} = \sum_{p=0}^{\frac{n-1}{2}} (-1)^p \frac{(n-p) \dots (n-2p)}{(p+1)!} \frac{f_{n+p}}{2^{2(p+1)} b_1 \dots b_{p+1} b_{n-p+1} \dots b_{n+1}} \quad (II)$$

Finally we will show that from the recurrent relation between the determinants D_p the value of

$$\lim_{n=\infty} \sqrt{\frac{f_n}{f_{n+1}}} = a$$

may be deduced. For the series

$$f_1 z + f_2 z^2 + f_3 z^3 + \dots$$

is converging when

$$\lim_{n=\infty} \left| \frac{f_{n+1}}{f_n} z^2 \right| < 1$$

or when

$$|z| < \lim_{n=\infty} \sqrt{\frac{f_n}{f_{n+1}}}$$

Now

$$\lim \sqrt{\frac{f_n}{f_{n+1}}} = \lim 2 \sqrt{\frac{b_1 \dots b_{n+1} D_{n-1}}{D_n}} = \alpha$$

therefore

$$\lim \frac{b_1 \dots b_{n+1} D_{n-1}}{D_n} = \left(\frac{\alpha}{2}\right)^2$$

$$\lim \frac{b_1 \dots b_{n+1} \cdot b_1 \dots b_n D_{n-2}}{D_n} = \left(\frac{\alpha}{2}\right)^4 \text{ etc.}$$

and finally

$$1 = \frac{\left(\frac{\alpha}{2}\right)^2}{b_1} - \frac{\left(\frac{\alpha}{2}\right)^4}{2! b_1 b_2} + \frac{\left(\frac{\alpha}{2}\right)^6}{3! b_1 b_2 b_3} - \text{etc.}$$

Hence it is evident that α is a root of the equation $I'(z) = 0$ as might be expected.

Astronomy. — “*Researches on the orbit of the periodic comet Holmes and on the perturbations of its elliptic motion.*”. By Dr. H. J. ZWIERS. (Communicated by Prof. H. G. VAN DE SANDE BAKHUIJZEN.)

In 1902, after the reappearance of the comet Holmes in 1899—1900 I published in full the results which I had derived from the investigation of the observations after its return.¹⁾ With the most accurate elements which I had been able to deduce from its appearance in 1892—93 I had calculated in advance the perturbations arising from the action of Jupiter and of Saturnus and at first also of the earth and thence I have derived a system of elements for 1899 September 9.0 mean time Greenwich, which served as a basis for an ephemeris published in No. 3553 of the *Astron. Nachrichten*. By means of this ephemeris the comet has been rediscovered at the Lick Observatory and the relatively small difference between the observed and the computed place proved that the elements of the

¹⁾ Recherches sur l'orbite de la comète périodique de Holmes et sur les perturbations de son mouvement elliptique, par Dr. H. J. ZWIERS. Deuxième mémoire. Leyde, E. J. Brill, 1902.

orbit found for 1892 and the computation of the perturbations which had been based on them were very nearly correct.

The observations in 1899 and 1900 furnished me with sufficient material to apply to the elements such small corrections as brought the remaining differences between the predicted and the observed positions within the limits of ordinary errors of observation. The system of elements obtained thus, which satisfied both the appearance of 1892—93 and that of 1899—1900 and which in my “*Deuxième Mémoire*” p. 78 has been recorded as “*Système VII*”, must naturally furnish the basis for further investigations. Therefore I shall give it here in its general features.

System VII.

Epoch 1899 June 11.0 mean time of Greenw.

Osculation 1899 September 9.0 „ „ „ „

$$M_0 = 22661'' 3264$$

$$\mu = 516'' 188791$$

$$\log a = 0.558 1320.0$$

$$\varphi = 24^\circ 17' 23'' 54$$

$$e = 0.4118532$$

$$i = 20^\circ 48' 9'' 84$$

$$\pi = 345 48 38.06 \left. \vphantom{\begin{matrix} \pi \\ \varpi \\ i \\ \pi \\ \varpi \end{matrix}} \right\} 1899.0$$

$$\varpi = 331 43 18.24$$

$$i = 20 48 10.29$$

$$\pi = 345 49 28.27 \left. \vphantom{\begin{matrix} \pi \\ \varpi \\ i \\ \pi \\ \varpi \end{matrix}} \right\} 1900.0$$

$$\varpi = 331 44 8.95$$

Although the corrections which had to be applied to the elements in consequence of the new observations were small, I immediately after the publication of those researches resolved to repeat the computation of the perturbations between 1892 and 1900 with the new elements and to extend it to all the planets of which the disturbing effect could not a priori be neglected as being insensible. This elaborate investigation, which necessarily required a new discussion of the two appearances of the comet, was however only partly finished when in 1905 the preparation for the third appearance had to be taken in hand.

I have then started from system VII, which though not perfect, yet satisfied all practical demands. I did not venture, however, to use those elements without more for the computation of the places at the return of the comet in 1906. It is true that the disturbing planets, especially Jupiter, whose influence is by far the greatest, remained at a considerable distance during the entire revolution of the comet, yet the feeble light of the comet in 1899—1900 and the difficulty

experienced by most observers to properly identify the comet in the midst of numerous faint nebulae near the apparent orbit, made me fear that such a rough ephemeris of the apparent places for 1906 might prove insufficient for rediscovering it and observing it.

In the autumn of 1905, I therefore resolved to derive the perturbations which the comet would suffer on its path between the perihelion passages of 1899 and 1906. The original plan of also computing the perturbations arising from the action of Saturnus had to be given up through lack of time. And so Jupiter remained the only disturbing planet. The method I chose was that of the variation of the elliptic constants; I also chose an interval of 80 days, because former investigations had shown that the accuracy, attainable by it was more than sufficient for my purpose. In former researches we have always adopted the rule that for each new epoch the small variations which the elements had undergone during the course of the last interval were to be applied to them. The computations required for this implied, however, an amount of labour not to be underrated, and as in this case the computations could have only a preliminary character I could leave aside these small corrections by which in this case only small quantities of the second order were neglected. Thus the above mentioned system VII was used as a basis for the computation of perturbations for the entire revolution. The places of the disturbing planet are taken from the Nautical Almanac; the longitudes only were reduced to the equinox of 1900.0 by applying the precession. The neglect of the small corrections for nutation and for the variation in the obliquity of the ecliptic cannot have any perceptible influence on the perturbations caused by the planet.

Instead of the elaborate tables of perturbations I shall for shortness communicate only the summed series, namely the quantities $II f$ for the mean daily motion and the quantities $I f$ for the other elements. By working out each table the reader will be able to form a judgment on the accuracy reached. The initial constants printed in big figures, which in the construction of the tables were derived from the first values of $\frac{dE}{dt}$, (E representing one of the 6 elements) and from their differences up to f^{IV} are chosen so that the integrals disappear for 1899 September 9 as lower limit. Up to 1900 February 16 the derivatives could be borrowed from the tables which I have communicated in my *Deuxième Mémoire* ps. 26—32; with regard, however to the interval chosen now I had to multiply $\frac{d\mu}{dt}$ by 4, and the other derivatives of the elements by 2.

TABLES OF THE JUPITER PERTURBATIONS.

Dates		i	δ	μ	M	π	φ
1899	Jan. 12	+ 4.536	+ 7.382	- 21.5730	+ 0.176	+ 13.677	- 29.200
	April 2	+ 2.690	+ 6.901	- 8.4814	+ 4.983	+ 6.957	- 16.151
	June 21	+ 0.760	+ 8.297	- 1.5328	+ 2.505	+ 2.601	- 4.611
	Sept. 9	- 0.625	- 3.826	+ 0.2787	- 2.530	- 3.150	+ 4.197
	Nov. 28	- 1.018	- 13.652	- 1.2125	- 5.973	- 13.460	+ 11.287
1900	Febr. 16	- 0.203	- 25.174	- 4.2367	- 6.752	- 28.616	+ 18.278
	May 7	+ 1.867	- 37.406	- 7.5053	- 5.822	- 47.169	+ 26.379
	July 26	+ 5.118	- 49.494	- 10.1533	- 4.954	- 67.123	+ 36.268
	Oct. 14	+ 9.397	- 60.732	- 11.6218	- 6.051	- 86.516	+ 48.205
1901	Jan. 2	+ 14.489	- 70.570	- 11.5478	- 10.874	- 103.621	+ 62.168
	Mrch 23	+ 20.135	- 78.624	- 9.6867	- 20.923	- 117.008	+ 77.946
	June 11	+ 26.049	- 84.681	- 5.8601	- 37.388	- 125.552	+ 95.199
	Aug. 30	+ 31.931	- 88.702	+ 0.0784	- 61.130	- 128.426	+ 113.505
	Nov. 18	+ 37.487	- 90.817	+ 8.2654	- 92.674	- 125.094	+ 132.387
1902	Febr. 6	+ 42.443	- 91.315	+ 18.8422	- 132.210	- 115.298	+ 151.341
	April 27	+ 46.560	- 90.624	+ 31.9635	- 179.598	- 99.047	+ 169.854
	July 16	+ 49.651	- 89.287	+ 47.8025	- 234.380	- 76.601	+ 187.427
	Oct. 4	+ 51.593	- 87.924	+ 66.5527	- 295.802	- 48.453	+ 203.590
	Dec. 23	+ 52.337	- 87.192	+ 88.4279	- 362.841	- 15.304	+ 217.927
1903	Mrch 13	+ 51.916	- 87.735	+ 113.6611	- 434.253	+ 21.975	+ 230.081
	June 1	+ 50.444	- 90.131	+ 142.5014	- 508.617	+ 62.385	+ 239.783
	Aug. 20	+ 48.115	- 94.838	+ 175.2122	- 584.410	+ 104.856	+ 246.855
	Nov. 8	+ 45.193	- 102.143	+ 212.0688	- 660.082	+ 148.314	+ 251.221
1904	Jan. 27	+ 41.996	- 112.115	+ 253.3579	- 734.136	+ 191.752	+ 252.903
	April 16	+ 38.875	- 124.566	+ 299.3790	- 805.216	+ 234.308	+ 252.011
	July 5	+ 36.183	- 139.032	+ 350.4492	- 872.176	+ 275.334	+ 248.718
	Sept. 23	+ 34.243	- 154.764	+ 406.9127	- 934.123	+ 314.438	+ 243.224
	Dec. 12	+ 33.309	- 170.745	+ 469.1545	- 990.396	+ 351.479	+ 235.703
1905	Mrch 2	+ 33.518	- 185.739	+ 537.6167	- 1040.430	+ 386.444	+ 226.250
	May 21	+ 34.834	- 198.384	+ 612.8073	- 1083.432	+ 419.129	+ 214.885
	Aug. 9	+ 36.981	- 207.384	+ 695.2691	- 1117.855	+ 448.580	+ 201.787
	Oct. 28	+ 39.372	- 211.929	+ 785.4184	- 1141.214	+ 472.756	+ 187.961
1906	Jan. 16	+ 41.116	- 212.537	+ 883.0549	- 1152.415	+ 490.526	+ 176.821
	April 6	+ 41.312	- 212.305	+ 986.3401	- 1158.665	+ 508.036	+ 173.909
	June 25			+ 1090.7414			

By means of these tables it is not difficult to integrate the perturbations for an arbitrary epoch according to the known expressions of the mechanical quadrature. As a new osculation epoch I have chosen

1906 January 16.0 mean time Greenwich

and I have found:

$$\begin{aligned}\Delta i &= + 40''34 & \Delta \varnothing &= - 3' 32''48 \\ \Delta \mu &= + 1''258874 & \iint \frac{d\mu}{dt} &= + 883''5368 \\ \Delta_1 M &= - 1147''7070 & \Delta \pi &= + 8' 2''08 \\ \Delta \varphi &= + 3' 2''01\end{aligned}$$

hence the new elements become:

epoch and osculation 1906 January 16.0 mean time Greenwich

$$\begin{aligned}M_o &= 1266412''143 \\ \mu &= 517''447665 \\ \log a &= 0.5574267.74 \\ \varphi &= 24^\circ 20' 25''55 \\ e &= 0.4121574 \\ i &= 20^\circ 48' 50''63 \\ \pi &= 345\ 57\ 30.35 \\ \varnothing &= 331\ 40\ 36.47\end{aligned} \left. \vphantom{\begin{aligned}M_o \\ \mu \\ \log a \\ \varphi \\ e \\ i \\ \pi \\ \varnothing\end{aligned}} \right\} 1900.0$$

From these disturbed elements we derive for the time of perihelion passage

1906 March 14.1804 mean time Greenwich

while the original system VII, without regard to the perturbations during the period since 1899 June would give

1906 March 13.8083.

If we take into account that the small retardation of not yet 9 hours is compensated by an increased longitude of the perihelion of 8', we find a posteriori confirmed, what could have been foreseen, that the perturbations during the second revolution have only slightly affected the places of the comet in space.

By reducing the elements i , π and \varnothing to the mean equinox of 1906.0 I find

$$\begin{aligned}i &= 20^\circ 48' 53''30 \\ \pi &= 346\ 2\ 31.63 \\ \varnothing &= 331\ 45\ 40.75\end{aligned} \left. \vphantom{\begin{aligned}i \\ \pi \\ \varnothing\end{aligned}} \right\} 1906.0.$$

In order to compute from these elements an ephemeris I have derived the following expressions for the heliocentric coordinates of the comet referred to the equator:

$$x = [9.993\ 7731.9] \sin (v + 77^\circ\ 37'\ 24''.85)$$

$$y = [9.876\ 2012.2] \sin (v - 20\ 58\ 31.25)$$

$$z = [9.832\ 7001.5] \sin (v - 1\ 47\ 16.19)$$

The coefficients in square brackets are logarithms; the quantity v denotes the true anomaly of the comet.

By means of the expressions above given the heliocentric coordinates have been derived from 4 to 4 days for mean noon at Greenwich; the coordinates of the sun were taken from the Nautical Almanac after having been reduced to the mean equinox of the beginning of the year. In the reduction of the mean places to apparent ones the aberration terms are omitted, because, as it is known, the influence of the aberration for the bodies of our solar system can be more simply accounted for by subtracting from the times of observation the equation of light. In the two following tables which contain the apparent places of the comet in α and δ I have therefore added in column ϑ for each date the equation of light expressed in mean solar days. The 4th column gives the logarithms of the geocentric distance. As first date I have chosen May 1st because I had derived from a preliminary computation that before that time there would be no chance to discover the comet owing to its small apparent distance from the sun and its large distance from the earth. The possibility did not seem excluded, however, that by means of powerful telescopes or sensitive photographic plates the comet might be discovered in January 1906. Therefore I have derived positions for that month and sent a short ephemeris to Prof. KREUTZ, who in a circular has communicated it to astronomers. To give a clear idea of the apparent orbit of the comet and also because the published places were not perfectly correct owing to a small reduction error, I here shall give the correct results from 4 to 4 days. Up to now (February 14) no tidings about the discovery have arrived, at which we need not wonder if we consider the cloudiness and especially the southern and generally unfavourable position.

The next table gives the apparent positions of the comet for the last 8 months of the year. The direct computations have been made from 4 to 4 days; between them one date has been interpolated taking into account the fourth differences.

As a measure for the probable brightness we generally calculate the quantity $H = \frac{1}{r^2 \rho^2}$. Although on account of the irregular variation of the comet's light it is not certain that the brightness will be

PLACES OF THE COMET BEFORE THE CONJUNCTION.

1906	apparent α	apparent δ	$\log \rho$	s	H
	^h ^m ^s	[°] ['] ["]			
Jan. 1	20 45 1.65	— 21 23 1.7	0.47858	0.017373	0.0230
5	53 18.18	— 20 26 48.1	.48066	456	.0229
9	21 1 33.24	— 19 29 15.1	.48257	533	.0229
13	9 46.66	— 18 30 24.6	.48431	603	.0228
17	17 58.35	— 17 30 17.8	.48590	668	.0228
21	26 8.26	— 16 28 58.8	.48733	726	.0228
25	34 16.26	— 15 26 28.4	.48860	778	.0227
29	42 22.19	— 14 22 50.3	.48971	824	.0227
Febr. 2	50 25.91	— 13 18 7.8	.49067	863	.0227
6	58 27.36	— 12 12 24.5	.49147	896	.0227
10	22 6 26.56	— 11 5 43.5	.49213	923	.0227

proportional to H , I for completeness have added this quantity to the table from 4 to 4 days. In 1892—93 this so-called “theoretical brightness” varied between 0.075 and 0.012.

Because the elements adopted for 1900 might still require small corrections, and as up to 1906 only the principal perturbation by Jupiter has been taken into account, it is not improbable that when the comet happens to be discovered there will be some difference between the observed and these computed places. In order to facilitate the search for astronomers who possess the needed instruments for finding it, I have repeated the calculation of the places first on the supposition that the comet will pass through its perihelion 4 days *earlier*, and secondly that it will pass 4 days *later* than would follow from the most probable elements. Although the adopted latitude of ± 4 days will probably be much larger than the real error in the accepted time of passage through the perihelion I give the results as obtained from direct calculation. The following table contains the variations in right ascension and declination for the two suppositions; column $\Delta \log \rho$ gives the corrections which would have to be applied to the 5th decimal of $\log \rho$ from the ephemeris communicated before.

(649)

APPARENT PLACES OF THE COMET FROM MAY 1 TO
DECEMBER 31, 1906,
FOR 0^h MEAN TIME AT GREENWICH.

1906	α	δ	$\log \rho$	z	H
	^h ^m ^s	[°] ['] ["]			
May 1	0 40 15.28	+ 12 49 44.3	0.47733	0.017 322	0.0240
3	44 0.82	+ 13 25 36.3	.47632	282	
5	47 46.23	+ 14 1 21.2	.47528	241	.0241
7	51 31.54	36 58.4	.47421	199	
9	55 16.77	+ 15 12 27.8	.47312	156	.0242
11	59 1.94	47 48.8	.47200	111	
13	1 2 47.03	+ 16 23 1.3	.47084	66	.0243
15	6 32.06	58 4.7	.46966	019	
17	10 17.02	+ 17 32 58.6	.46844	0.016 972	.0244
19	14 1.90	+ 18 7 42.8	.46719	923	
21	17 46.67	42 16.7	.46591	873	.0246
23	21 31.32	+ 19 16 39.8	.46460	822	
25	25 15.84	50 51.9	.46326	770	.0247
27	29 0.20	+ 20 24 52.4	.46189	717	
29	32 44.40	58 40.9	.46048	663	.0248
31	36 28.40	+ 21 32 17.0	.45904	608	
June 2	40 12.22	+ 22 5 40.5	.45757	552	.0250
4	43 55.83	38 51.0	.45607	495	
6	47 39.23	+ 23 11 48.3	.45453	437	.0252
8	51 22.42	44 32.1	.45296	378	
10	55 5.37	+ 24 17 2.4	.45137	317	.0253
12	58 48.06	49 18.9	.44974	256	
14	2 2 30.46	+ 25 21 21.5	.44807	194	.0255
16	6 12.51	53 9.8	.44637	131	
18	9 54.18	+ 26 24 43.6	.44464	67	.0257
20	13 35.40	56 2.8	.44287	001	
22	17 16.13	+ 27 27 7.1	.44107	0.015 935	.0259
24	20 56.31	57 56.2	.43923	868	
26	24 35.89	+ 28 28 30.0	.43736	799	.0261

1906	α	δ	$\log p$	s	H
	^h ^m ^s	^o ['] ["]			
June 28	2 28 14.81	+ 28 58 48.2	0.43545	0.015 730	
	31 53.03	+ 29 28 50.8	.43350	660	0.0264
July 2	35 30.49	58 37.7	.43152	589	
4	39 7.15	+ 30 28 8.8	.42951	517	.0266
6	42 42.95	57 24.2	.42746	444	
8	46 17.85	+ 31 26 24.1	.42538	370	.0269
10	49 51.75	55 8.4	.42326	295	
12	53 24.59	+ 32 23 37.4	.42111	219	.0271
14	56 56.26	51 50 9	.41892	143	
16	3 0 26.67	+ 33 19 49.1	.41669	665	.0274
18	3 55.70	47 32.1	.41442	0.014 987	
20	7 23.24	+ 34 14 59.8	.41212	907	.0277
22	10 49.18	42 12.4	.40978	827	
24	14 13.40	+ 35 9 9.8	.40740	746	.0281
26	17 35.80	35 52.2	.40499	665	
28	20 56.25	+ 36 2 19.8	.40254	582	.0284
30	24 14.64	28 32.6	.40006	499	
Aug. 1	27 30.86	54 31.0	.39755	416	.0288
3	30 44.79	+ 37 20 15.2	.39500	331	
5	33 56.32	45 45.6	.39241	246	.0291
7	37 5.28	+ 38 11 2.7	.38979	160	
9	40 11.54	36 6.8	.38714	074	.0295
11	43 14.91	+ 39 0 58.0	.38446	0.013 988	
13	46 15.20	25 36.8	.38174	900	.0300
15	49 12.25	50 3.3	.37899	813	
17	52 5.84	+ 40 14 17.8	.37621	724	.0304
19	54 55.77	38 20.5	.37340	636	
21	57 41.84	+ 41 2 11.5	.37057	547	.0308
23	4 0 23.84	25 50.9	.36771	458	
25	3 1.59	49 19.0	.36482	369	.0313
27	5 34.86	+ 42 12 35.9	.36191	280	

1906	α	δ	$\log \rho$	z	H
	^h ^m ^s	[°] ['] ["]			
Aug. 29	4 8 3.48	+ 42 35 41.8	0.35899	0.013 191	0.0318
31	10 27.94	58 36.9	.35605	102	
Sept. 2	12 45.92	+ 43 21 21.3	.35308	013	.0323
4	14 59.28	43 55.4	.35010	0.012 924	
6	17 7.07	+ 44 6 19.0	.34712	835	.0329
8	19 9.03	28 32.3	.34412	747	
10	21 4.88	50 35.1	.34112	659	.0334
12	22 54.34	+ 45 12 27.0	.33812	572	
14	24 37 12	34 7.7	.33512	485	.0339
16	26 12.92	55 36 6	.33212	399	
18	27 41.47	+ 46 16 53.0	.32913	314	.0345
20	29 2.48	37 56.1	.32615	230	
22	30 15.71	58 44.9	.32320	147	.0350
24	31 20.90	+ 47 19 18.3	.32027	066	
26	32 17.81	39 35.2	.31737	0.011 985	.0356
28	33 6.20	59 34.3	.31450	907	
30	33 45.85	+ 48 19 14.3	.31168	830	.0361
Oct. 2	34 16.56	38 33.8	.30891	754	
4	34 38.08	57 31.0	.30618	681	.0366
6	34 50.16	+ 49 16 3.6	.30351	609	
8	34 52.61	34 9.6	.30092	540	.0370
10	34 45.25	51 46.5	.29840	473	
12	34 27.94	+ 50 8 51.4	.29595	409	.0375
14	34 0.56	25 21.4	.29359	347	
16	33 23.06	41 13.3	.29134	288	.0378
18	32 35.43	56 23.7	.28919	232	
20	31 37.75	+ 51 10 49.1	.28715	180	.0381
22	30 30.16	24 26.0	.28523	130	
24	29 12.87	37 11.0	.28345	085	.0383
26	27 46.15	49 0.8	.28181	043	
28	26 10.32	59 51.9	.28031	005	.0384

1906	α	δ	$\log p$	q	H
	^h ^m ^s	[°] ['] ["]			
Oct. 30	4 24 25.75	+ 52 9 41.1	0.2789	0.010 971	
Nov. 1	22 32.88	18 25.1	.27779	941	0.0384
3	20 32.19	26 0.8	.27678	916	
5	18 24.26	32 25.2	.27595	895	.0383
7	16 9.72	37 35.5	.27530	879	
9	13 49.28	41 29.2	.27484	867	.0380
11	11 23.70	44 4.0	.27457	861	
13	8 53.82	45 18.4	.27451	859	.0376
15	6 20.53	45 11.0	.27466	863	
17	3 44.79	43 41.2	.27502	872	.0371
19	1 7.59	40 48.9	.27560	886	
21	3 58 29.91	36 35.1	.27640	906	.0365
23	55 52.74	31 1.1	.27742	932	
25	53 17.00	24 8.9	.27865	963	.0357
27	50 43.59	16 0.8	.28010	0.011 000	
29	48 13.36	6 39.9	.28178	042	.0848
Dec. 1	45 47.10	+ 51 56 9.2	.28368	090	
3	43 25.56	44 32.6	.28578	144	.0337
5	41 9.42	31 53.9	.28810	204	
7	38 59.30	18 17.3	.29062	269	.0326
9	36 55.80	3 47.5	.29334	340	
11	34 59.40	+ 50 48 29.0	.29627	417	.0314
13	33 10.58	32 26.7	.29939	499	
15	31 29.73	15 45.9	.30270	587	.0302
17	29 57.19	+ 49 58 31.6	.30619	681	
19	28 33.19	40 49.1	.30984	779	.0289
21	27 17.93	22 43.8	.31365	883	
23	26 11.50	4 20.5	.31763	993	.0275
25	25 13.95	+ 48 45 43.9	.32175	0.012 107	
27	24 25.22	26 58.7	.32601	220	.0262
29	23 45.29	8 8 8	.33039	350	
31	23 14.07	+ 47 49 18.0	.33489	479	.0249

VARIATIONS OF α , δ AND $\log \rho$ FOR THE ALTERED TIME OF PASSAGE
THROUGH THE PERIHELION.

1906	$T = -4$ days			$T = +4$ days		
	$\Delta \alpha$	$\Delta \delta$	$\Delta \log \rho$	$\Delta \alpha$	$\Delta \delta$	$\Delta \log \rho$
May 5	+ 3 ^m 13.48	+ 38' 55.2"	+ 231	- 3 ^m 13.42	- 39' 27.7"	- 233
21	+ 3 22.15	+ 36 23.2	+ 294	- 3 22.12	- 37 3 8	- 297
June 6	+ 3 33.07	+ 33 10.6	+ 355	- 3 33.23	- 33 58.3	- 359
22	+ 3 46.12	+ 29 19.9	+ 413	- 3 46.62	- 30 13.4	- 418
July 8	+ 4 1.25	+ 24 55.8	+ 469	- 4 2.30	- 25 53.4	- 476
24	+ 4 18.58	+ 20 4.1	+ 521	- 4 20.42	- 21 4.4	- 529
Aug. 9	+ 4 38.61	+ 14 54.2	+ 567	- 4 41.55	- 15 55.9	- 576
25	+ 5 2 49	+ 9 39.3	+ 606	- 5 6.87	- 10 41.7	- 616
Sept. 10	+ 5 31.97	+ 4 41.9	+ 632	- 5 38.29	- 5 45.9	- 642
26	+ 6 9.74	+ 39.2	+ 640	- 6 18.02	- 1 49.1	- 649
Oct. 12	+ 6 55.91	- 1 27.1	+ 621	- 7 5.99	+ 4.1	- 627
28	+ 7 44.03	- 23.3	+ 566	- 7 54.54	- 1 20.9	- 569
Nov. 13	+ 8 15.71	+ 4 15.2	+ 475	- 8 23.95	- 6 19.7	- 474
29	+ 8 10.71	+ 10.42.4	+ 361	- 8 14.80	- 12 50.9	- 356
Dec. 15	+ 7 29.94	+ 15 44.7	+ 247	- 7 30.69	- 17 37.3	- 241

Leyden, January 1906.

Physics. — “*On the motion of a metal wire through a lump of ice*”.

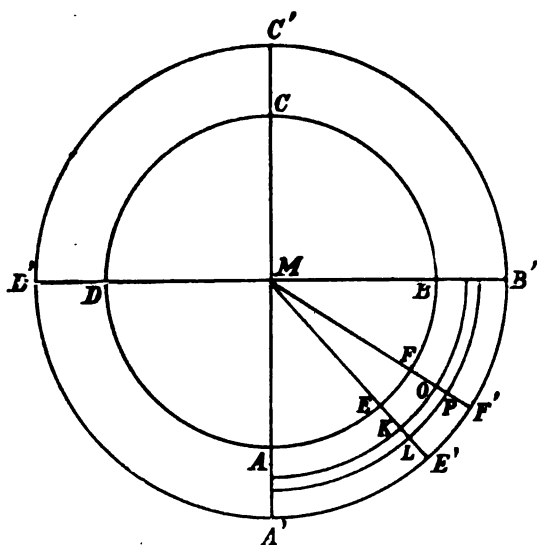
By L. S. ORNSTEIN. (Communicated by Prof. H. A. LORENTZ).

In a well known experiment on the regelation of ice a metal wire charged with weights is placed on a lump of ice. It moves slowly through the ice, while on the upper side new ice is formed; after a short time the motion takes place with uniform velocity. This phenomenon is explained by the fact, that if we increase the pressure the meltingpoint is lowered.

In order to calculate the velocity of the wire I shall consider an infinite circular cylinder which is moved through an infinite lump

of ice by a force perpendicular to its axis. The phenomenon is the same in each normal section. I suppose round the wire a layer of water whose thickness is small in comparison with the diameter of the wire. At the bounding surface of water and ice there is a pressure, which decreases from the lower to the upper side of the boundary. This pressure depends on the force by which the wire is acted on pro unit of length. As the motion is very slow the temperature in each point may be supposed to be the meltingpoint corresponding to the pressure existing in the point. The flow of heat, determined by the distribution of temperature is the same as if the wire were at rest. At the upperside of the bounding surface of ice and water heat flows away and water is frozen, at the lower side the ice is melted by the heat that is carried towards the surface. If we can determine the quantity that is melted we shall be able to determine the velocity acquired by the wire.

Let M be the centre of the circular section of the wire and R the radius, the boundary between ice and water being a circle of radius $R + d$.



The pressure at the circle $A'B'C'$ in any point E' may be represented by the formula

$$p = p_0 + b \cos \varphi,$$

φ being the angle between the radius ME' and the line MA which has been taken for axis of ordinates. The corresponding temperature is

$$t = t_0 + b \left(\frac{dt}{dp} \right)_0 \cos \varphi,$$

$\left(\frac{dt}{dp} \right)_0$ being the change of

the meltingpoint per unit increase of pressure near 0°C .

Let k_1 , be the coefficient of conductivity within the circle ABC , k_2 that of the layer of water, and k_3 that of the ice without $A'B'C'$.

The differential equation for the temperature is in every one of these fields

$$\frac{\partial^2 t}{\partial x^2} + \frac{\partial^2 t}{\partial y^2} = 0.$$

The conditions at the limits of the fields are:

1. at ABC $t_1 = t_2, \quad k_1 \left(\frac{\partial t_1}{\partial n} \right)_1 = k_2 \left(\frac{\partial t_2}{\partial n} \right)_2,$

2. at $A'B'C'$ $t_2 = t_3 = t_0 + b \left(\frac{dt}{dp} \right)_0 \cos \varphi,$

3. at infinite distance $t_3 = t_0.$

The normal at ABC coinciding with the radius.

The formulae:

$$t_1 = t_0 + B_1 r \cos \varphi \quad \text{in the wire,}$$

$$t_2 = t_0 + B_2 r \cos \varphi + \frac{C_2}{r} \cos \varphi \quad \text{in the layer of water,}$$

$$t_3 = t_0 + \frac{C_3}{r} \cos \varphi \quad \text{in the surrounding ice}$$

satisfy the equations r being the distance from the point M . For the coefficients I find the relations

$$B_1 = B_2 + \frac{C_2}{R^2},$$

$$k_1 B_1 = k_2 \left(B_2 - \frac{C_2}{R^2} \right)$$

$$B_2 + \frac{C_2}{(R+d)^2} = \frac{C_3}{(R+d)^2} = b \left(\frac{dt}{dp} \right)_0 \frac{1}{R+d}.$$

Neglecting powers of d/R I find

$$\frac{C_2}{R^2} = - \frac{b \left(\frac{dt}{dp} \right)_0 (k_1 - k_2)}{2(R+d)\{k_2 + d/R(k_1 - k_2)\}},$$

$$B_2 = \frac{b \left(\frac{dt}{dp} \right)_0 (k_1 + k_2)}{2(R+d)\{k_2 + d/R(k_1 - k_2)\}}.$$

For an element $E'F'$ of $A'B'C'$ the flow of heat into the ice towards the surfaces amounts to:

$$- k_2 \frac{C_2}{R+d^2} \cos \varphi d\varphi,$$

if we write $d\varphi$ for the angle $E'MF'$. Hence the total quantity of heat conducted through the ice towards the surface $A'B'$ per unit of time:

$$- k_2 b \left(\frac{dt}{dp} \right)_0 \int_0^{\pi/2} \cos \varphi d\varphi = - k_2 b \left(\frac{dt}{dp} \right)_0.$$

In the layer of water the flow of heat per unit of time is for $E'F'$

$$-(R+d) d\varphi \cos \varphi k_1 \left(B_1 - \frac{C_1}{(R+d)^2} \right)$$

and for $A'B'$ totally

$$-k_2 (R+d) \left(B_1 - \frac{C_1}{(R+d)^2} \right) = -k_2 b \left(\frac{dt}{dp} \right)_0 \frac{k_1 - (k_1 - k_2)d/R}{k_2 + (k_1 - k_2)d/R}.$$

Of course as much heat is lost at the surface $B'C'$ as is conducted towards $A'B'$; and the melted and frozen quantities of ice and water will therefore be equal. W being the quantity of heat that is required for the melting of a gramme of ice, the melted quantity is

$$- \frac{2 \left[k_1 \frac{k_1 - d/R(k_1 - k_2)}{k_2 + d/R(k_1 - k_2)} + k_2 \right] b \left(\frac{dt}{dp} \right)_0}{W}.$$

If S_y is the specific gravity of ice, the volume of this quantity is:

$$- \frac{2 \left[k_1 \frac{k_1 - d/R(k_1 - k_2)}{k_2 + d/R(k_1 - k_2)} + k_2 \right] \left(\frac{dt}{dp} \right)_0 b}{W S_y}.$$

On the other hand, if the cylinder moves with a uniform velocity v a volume

$$2 R v.$$

is melted. So we find for the value of v

$$v = - \frac{\left[k_1 \frac{k_1 - d/R(k_1 - k_2)}{k_2 + d/R(k_1 - k_2)} + k_2 \right] \left(\frac{dt}{dp} \right)_0 b}{R W S_y}.$$

To express b in the force P acting per unit of length of the cylinder we have only to notice that an element $EF = R d\varphi$ is acted on by a force per unit of surface $p \cos \varphi = (p_0 + b \cos \varphi) \cos \varphi$. Hence:

$$P = 2 \int_0^\pi (p_0 \cos \varphi + b \cos^2 \varphi) R d\varphi = \pi b R$$

The velocity C in case $P = 1$ is found to be

$$C = - \frac{\left(\frac{dt}{dp} \right)_0 \left[k_1 \frac{k_1 - d/R(k_1 - k_2)}{k_2 + d/R(k_1 - k_2)} + k_2 \right]}{\pi R^2 W S_y} \quad \dots \quad (I).$$

We can find another expression for d/R if we pay attention to the motion of the water. If we conceive the wire to be at rest but the ice moving along it, we shall see at the limit $A'B'$ water continually streaming into the channel $ABA'B'$ while it streams out of

it and freezes at the part $B'C'$ of the surface. The velocity of the ice being v we find for the quantity of water entering through EF'

$$(R + d) v \cos \varphi d\varphi.$$

This is also the difference between the quantities flowing across FF' and EE' upwards.

This quantity can also be determined by means of the hydrodynamical equations. Take for axis of ξ a circle with radius $R + \frac{1}{2}d$ and for axis of η a radius of the circle. The forces acting on an element $KLOP$ are in equilibrium. Writing u_ξ for the velocity parallel to the axis of ξ , μ for the coefficient of viscosity, neglecting the velocity u_η and taking the intersection of the ξ circle, with EE' for origin of coordinates we have:

$$\mu \frac{\partial^2 u_\xi}{\partial \eta^2} = - \frac{b \sin \varphi}{R}.$$

At the circle AB , $u_\xi = 0$, at $A'B'$, $u_\xi = v \sin \varphi$, therefore:

$$\mu u_\xi = - \frac{b \sin \varphi \eta^2}{2R} - \frac{v \sin \varphi}{d} \eta + \frac{\sin \varphi}{2} \left(v + \frac{b d^2}{4R} \right)$$

and the quantity streaming across EE' is

$$\int_{-d/2}^{+d/2} u_\xi d\eta = \frac{1}{\mu} \left\{ \frac{bd^3}{12R} + \frac{vd}{2} \right\} \sin \varphi,$$

the difference between the quantities of water flowing across FF' and EE' will therefore be

$$\frac{1}{\mu} \left\{ \frac{b d^3}{12 R} + \frac{vd}{2} \right\} \cos \varphi d\varphi$$

and we have, neglecting powers of d/R :

$$v = \frac{b d^3}{12 \mu R^2} \dots \dots \dots (II^a)$$

In the experiments the wires become curved. I suppose the wire to be perfectly flexible and the stress to have the same value S in all its parts; the force per unit of length perpendicular to the wire is given in each point by

$$S \frac{d\omega}{ds},$$

$d\omega$ being the angle between two consecutive tangents to the curve. The curvature being not large we can use the coefficient given by (I) to find the normal velocity arising from this force. This velocity is

$$C S \frac{d\omega}{ds}.$$

In a time dt the element ds of the wire describes a surface

$$C S \frac{d\omega}{ds} ds dt.$$

If the wire at the ends is vertical the whole wire will therefore describe an area

$$dt \int_0^\pi C S \frac{d\omega}{ds} ds = \pi C S dt.$$

Now if the velocity of the wire is v , and the distance between the vertical ends d_1 , the same area will be vd_1 so that we have

$$v = \frac{\pi C S}{d_1} \quad \dots \dots \dots (III)$$

or if the angle between the ends is 2α , and P the weight at each end,

$$v = \frac{2\alpha C P}{d_1 \sin \alpha} \quad \dots \dots \dots (III_a)$$

We shall next consider the form taken by the wire if it descends as a whole with uniform velocity. It is determined by the condition

$$C S \frac{d\omega}{ds} = v \frac{dx}{ds},$$

or

$$\frac{d\omega}{ds} = \frac{\pi}{d_1} \frac{dx}{ds}$$

As $\rho d\omega = ds$, ρ being the radius of curvature, this equation becomes

$$\frac{\frac{d^2 y}{dx^2}}{1 + \left(\frac{dy}{dx}\right)^2} = \frac{\pi}{d_1}.$$

Taking the axis of x horizontal at the highest point of the line, the axis of y vertical downwards we have for $x = 0$,

$$y = 0 \quad \frac{dy}{dx} = 0$$

therefore

$$\frac{dy}{dx} = \tan \frac{\pi}{d_1} x,$$

$$\cos \frac{\pi}{d_1} x = e^{-\frac{\pi}{d_1} y}.$$

The normal pressure at the highest point is

$$S_n = \frac{S\pi}{d_1}$$

In order to find the formula (II^a) for curved wires we can put, approximately, for b its value at the point $x = 0$ $y = 0$.

So that we may put for

$$b = \frac{S_n}{\pi R} = \frac{S}{Rd_1}.$$

By this the formula (II^a) gives

$$v = \frac{S}{12\mu d_1} \left(\frac{d}{R} \right)^3 \dots \dots \dots (II^b)$$

S being equal to the weight hanging at each end.

If the angle between the tangents at the ends is 2α , we have other formulae. The equation of the curve becomes

$$\cos \frac{2\alpha}{d_1} x = e^{-\frac{2\alpha}{d_1} y},$$

and the velocity, if P is again the weight at each end

$$v = \frac{2\alpha CP}{d_1 \sin \alpha} \dots \dots \dots (III^a)$$

By the hydrodynamical method the same velocity is found to be

$$v = \frac{2\alpha P}{12\pi\mu d_1 \sin \alpha} \left(\frac{d}{R} \right)^3 \dots \dots \dots (II^c)$$

Dr. J. H. MEERBURG has made a series of experiments, of which he will communicate the results at a later opportunity. The agreement with the theory is not very satisfactory. It must be noticed however that d is very small. The roughness of the surface of the wire will therefore greatly increase the resistance to the motion of the water, so that the result of the hydrodynamical method can no longer be considered as correct.

Zoology. — “*On the Polyandry of Scalpellum Stearnsi*” by P. P. C. HOEK.

One of the largest forms of the genus *Scalpellum* which is so rich in species is *Scalpellum Stearnsi*, PILSBRY from shallow water near the coast of Japan.

This species is represented by two varieties or sub-species in the collection of Cirripedes made by the Siboga Expedition in the waters of the Dutch East Indies and handed over to me for description. Both forms agree in the main with PILSBRY's species — they differ, however,

in some regards from one another as well as from the Japan species. I made the acquaintance of the latter by studying a few samples which were kindly lent me from the Berlin museum by the Director (Prof. K. MOEBIUS) and by the curator of the Crustacea Department (Prof. W. WELTNER).

Apart from PILSBRY¹⁾, the Japan species has also been named and described by FISCHER²⁾; one of the two varieties from the Malay Archipelago has of late again met with the same fate from ANNANDALE³⁾, who tried to introduce it into the literature of the Cirripedia as a new species.

Yet, though we dispose at present of three names and three fairly extensive descriptions for this species, a very curious phenomenon in the life-history of the reproductive period of this *Scalpellum* has hitherto escaped the attention of its describers; for I can hardly believe that they could have discovered this peculiarity and yet not mentioned it in their papers.

PILSBRY says of this species (and FISCHER in this regard quite agrees with him) that it was found in shallow water in Japan. The specimens of the Berlin Museum were from Nagasaki and apparently also from coastal waters. Those of the Siboga Expedition are from four different stations the depths of which range from 204 to 450 m. ANNANDALE had a single specimen at his disposal, caught in Bali Straits at a depth of 160 fathoms, about 290 m.

Scalpellum Stearnsi belongs to the unisexual species of the genus: the large specimens with fully developed capitulum of a length of about 5 cm. and with (for a species of *Scalpellum*) very long peduncles (of 5—9 cm. length) are the females. The males (which should not be called "complemental" males in this case) are looked for in vain at the place they ordinarily occupy, viz., at the inner side of the scutum, near the occludent margin, a little in front of or above the adductor muscle, in a duplicature of the sac or mantle which covers the valves of the capitulum on their inner surface. They are not to be found there — and I think this explains why they escaped the attention of the earlier describers. DARWIN discovered that the little males in one of the species (in *Sc. rostratum*, DARWIN) were attached as three little parasites to the body of the hermaphrodite, close under the labrum, between it and the adductor muscle almost in the median line of the body — but even at that place they are not

¹⁾ Proceed. Acad. Nat. Sci. Philadelphia. 1890. p. 441—443.

²⁾ Bullet. Soc. Zool. d. France. XVI. 1891. p. 116—118.

³⁾ Memoirs Asiatic Soc. of Bengal. I. N^o. 5. 1905. p. 74—77.

to be found in *Sc. Stearnsi*. I noted, however, that that part of the sac or mantle, which unites the two scuta behind or beneath the adductor muscle and which can be better seen by moving the two scuta slightly from one another, in the largest and oldest specimen of the collection, showed a crusty and grainy surface — just as if a *Flustra* or other Bryozoon were attached to it. Investigating a part of that crusty covering I easily found that each grain represented a male and that over a hundred of these were attached to the same female. Each male is inclosed in a kind of capsule (a thickening of the mantle) and that part of the mantle-surface which is opposite the head-end with the prehensile antennae forms a little elevation over the surface of the capsule. They are in parts so closely placed as to flatten one another mutually. Their dimensions are 0.7×0.5 mm. — they are even small for males of *Scalpellum*. Their structure agrees with that of the males of several other species of this genus: round about the opening of the mantle, at the extremity of the little elevation over the surface of the chitinous capsule, four rudimentary valves are observed. What I think, so far as my experience goes, is characteristic for this species, is that short rudimentary tentacles are attached to the surface of the mantle between (alternating with) the small valves, little appendages — which of course have nothing in common with the articulated antennae or other limbs of the Cirripedes. Should any doubt remain, as to whether these little parasites really represented the males of this species, these tentacles might be used to dissipate it. A few small, quite young females, in which the capitulum however was already furnished with calcareous valves and the whole appearance of which corresponded with an early condition of fullgrown females, were found attached to the surface of the capitulum of one of the large specimens. Now, these little females are furnished with the same tentacles. They are embryological organs, which of course may have importance from a morphological or phylogenetic point of view, but which have disappeared in the fullgrown females. In the young females they occupy the same place as in the males, viz. at the free extremity (the tip) of the capitulum attached to the chitinous surface between the two calcareous plates which represent the terga, near the anterior extremity of the orifice — in the females large, in the males relatively much smaller — which gives entrance to the cavity in which the animal's body is lodged.

I do not believe that examples are known in animals so highly developed as Cirripedia of such a pronounced polyandry as in this species of *Scalpellum*. As a rule, the number of males found attached

to the capitulum of the female or of the hermaphrodite is one at each side only, in some species it is two or three and the largest number I have observed was five. How can we explain that there is a species with such a large number as the case mentioned? I have tried in vain to find an explanation. We do not know much of the habits of these animals. It is hardly admissible that the great number of males should be connected with the depth at which they live, for (1) the same species which is found in the Malay Archipelago at a depth of 200—400 m. lives in the Japan sea in shallow water, and (2) we know species living in coastal waters and others found in depths of over 1800 m., all of which have two males only. A connection exists no doubt between the place where the little males are found attached and their great number — but I am at a loss to understand what the relation may be. The eggs of these Cirripedes are fecundated at the moment they are excluded and form two leaves (the so-called ovigerous lamellae) which remain in the sack or mantle-cavity of the female until the eggs hatch out. If the males are attached at the margin of the mantle-cavity, the chance that the eggs will be impregnated is of course larger than in the case when they are attached at a greater distance, as in *Sc. Stearnsi*. So it is easily understood that in the latter case a greater number of males would be required — but why did they choose for attachment a place which is less favourable for impregnation? Because they were so numerous and did not find space enough at the ordinary place?

Mathematics. — “*A group of complexes of rays whose singular surfaces consist of a scroll and a number of planes*”. By Prof. JAN DE VRIES.

1. The generatrices of a rational scroll can be arranged in the groups of an involution I_p ; to this end we have but to arrange their traces on an arbitrary plane in the groups of an I_p . If we consider each pair of lines l, l' of I_p as directrices of a linear congruence, it immediately occurs to us to examine the complex of rays Γ which is the compound of the ∞^1 congruences determined by it.

Let the scroll q^n be of order n and let it have an $(n-1)$ -fold directrix d . The generatrices l form a fundamental involution I_{n-1} , each group of which consists of the $(n-1)$ right lines, coinciding in a point of d . This I_{n-1} has evidently $(n-2)(p-1)$ pairs in

common with the given I_p ; so on d lie as many points of intersection H of pairs l, l' of the involution I_p . Each ray through a point H belongs to the complex Γ , likewise each ray in the connecting plane h of the right lines l, l' ; i. o. w. the complex has $(n-2)(p-1)$ principal points H and $(n-2)(p-1)$ principal planes h .

2. On an arbitrary plane α a rational curve c^n with $(n-1)$ -fold point D is determined by φ^n . The rays of the complex lying in α envelop a curve (α) of class $(n-1)(p-1)$, the curve of involution (director curve) of I_p in which the points of c^n are arranged by the given I_p .¹⁾

So the complex is of order $(n-1)(p-1)$.

The line of intersection of α with a principal plane h being a ray of Γ , the curve of the complex (α) touches all principal planes.

If α is made to pass through a right line l of φ^n , then (α) splits up into the pencils having for vertices the traces L' of the $(p-1)$ rays conjugate to l and into a curve of order $(n-2)(p-1)$, the curve of the involution of T_p on the curve c^{n-1} which α has in common with φ^n besides. So a tangent plane of φ^n is a singular plane of Γ .

The singular surface consists of a scroll and the principal planes.

When a tangent plane contains one of the principal points it passes in general through the directrix d , therefore through all principal points. Then (α) splits up into $(n-2)(p-1)$ pencils (H) and $(p-1)$ pencils (L') .

Of the $n-1$ generatrices l through a point H , two, l_0 and l_∞ , form a pair of I_p . If we bring α through one of the remaining right lines l_k ($k=1$ to $n-3$), then (α) consists of $(p-1)$ pencils with vertices L'_k , the pencil (H) and a curve of class $(n-2)(p-1)-1$.

In an arbitrary plane through H the curve of the complex (α) consists of the pencil (H) and a curve of order $(n-1)(p-1)-1$.

3. The rays of the complex through an arbitrary point A envelop a cone (A) of order $(n-1)(p-1)$ passing through the principal points.

If A lies on φ^n cone (A) consists of $(p-1)$ concentric pencils and a cone of order $(n-2)(p-1)$.

If we assume A in a principal plane h then only *one* pencil separates itself from the cone of the complex.

¹⁾ I_p has $(n-1)(p-1)$ pairs in common with the involution I_n which an arbitrary pencil determines on c^n .

If A is taken on the line of intersection of two planes h , two pencils are separated from the cone. Three pencils are obtained when A is point of intersection of three principal planes.

If we take A on the curve c^{n-2} which a plane h has in common with φ^n then (A) consists of p concentric pencils and a cone of order $(n-2)(p-1)-1$.

If A is a point of intersection of φ^n with two principal planes the number of pencils evidently becomes $(p+1)$.

4. The curve of the complex (α) is of order $(p-1)(2n+p-6)^1$. It possesses $\frac{1}{2}(p-1)(p-2)(n-2)$ threefold tangents ²⁾ which are transversals of as many triplets of right lines belonging to a group of I_p . The cone of the complex (A) possessing evidently as many threefold edges, the scrolls each having three conjugate right lines l as directrices form together a congruence γ of order and class $\frac{1}{2}(p-1)(p-2)(n-2)$.

Each principal point H is for this congruence a *singular point* of order $(p-2)$; the *singular cone* is broken up into $(p-2)$ pencils.

Each principal plane h is a *singular plane* of order $(p-2)$ and contains $(p-2)$ pencils of rays of congruence.

5. The right lines resting on four lines l belonging to a group of I_p form a scroll enclosed in Γ , of which the order is going to be determined.

Each transversal t of three conjugate right lines l_1, l_2, l_3 and the arbitrary right line a intersects still $(n-3)$ generatrices m of φ^n . To each of these right lines m can be made to correspond the $(p-3)$ right lines l' forming with l_1, l_2, l_3 a group of I_p .

To each ray l' belong $(p-1)$ triplets l_1, l_2, l_3 , so $2(p-1)$ transversals t and therefore $2(n-3)(p-1)$ rays m .

The congruence $(1, 1)$ of the right lines resting on m and a has with the congruence γ in common $(n-2)(p-1)(p-2)$ rays t , so that to m are conjugate $(n-2)(p-1)(p-2)(p-3)$ right lines l' .

Now each transversal of four lines l belonging to a group of I_p evidently gives four coincidences of the correspondence (l', m) .

¹⁾ The characteristic numbers of the curve of involution of an I_p on a rational c^n are found in the dissertation of JOH. A. VREESWIJK JR. (Involuties op rationale krommen, Utrecht 1905, page 38).

²⁾ See also my paper "Complexes of rays in relation to a rational skew curve" (These Proceedings, VI, page 12).

• Consequently the scroll of the transversals of quadruplets of the involution is of order $\frac{1}{12}(p-1)(p-2)(p-3)(4n-9)$.

Each principal point and each principal plane of Γ bears $\frac{1}{2}(p-2)(p-3)$ right lines of this scroll.

6. If φ^n possesses also a single directrix e all principal planes of Γ pass through e and the complex is in itself dual.

If φ^n has a nodal curve σ of order $\frac{1}{2}(n-2)(n-1)$ each generatrix l rests in $(n-2)$ points on σ , and is thus cut by $(n-2)$ right lines l . By this the generatrices are arranged in a symmetric correspondence of order $(n-2)$, having with l_p given on φ^n in common $(n-2)(p-1)$ points H . So the complex has again $(n-2)(p-1)$ principal points and as many principal planes.

In like manner the order of Γ remains the same. But now the curve of the complex can break up on account of its plane containing two or three principal points by which two or three pencils are separated. Besides α can contain still a right line l . So here the degenerations of (α) are dually opposed to those of the cone (A) .

(February 21, 1906).

KONINKLIJKE AKADEMIE VAN WETENSCHAPPEN
TE AMSTERDAM.

PROCEEDINGS OF THE MEETING
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Physics. — "*A new method for determining the rate of decrease of the radiating power from the center toward the limb of the solar disk*". By Prof. W. H. JULIUS.

(Communicated in the Meeting of January 27, 1906)

The brightness of the solar disk is known to diminish considerably from the center toward the limb. Although this prominent feature of the solar phenomenon should be among the first accounted for in every theory of the Sun, it leads to problems presenting so many difficulties, that a satisfactory explanation is, until now, altogether wanting. And even the empirical study of the law according to which the radiating power varies across the disk, is not very advanced.

What we know about the question is founded on researches in

which either a photometer, or a thermopile, a bolometer or a radio-micrometer was used for exploring an *image* of the Sun. The results obtained by different observers are rather discordant¹⁾. This may be partly due to instrumental or accidental errors, but there is also a systematical error which must have influenced similarly all of the results thus obtained, and which proceeds from the scattering of the rays by the terrestrial atmosphere. In any point of an image of the Sun is not only to be found the radiation coming from the corresponding point of the disk, but, besides, some diffused radiation proceeding from other parts of the disk. This disturbing effect will, of course, vary in magnitude with the condition of our atmosphere, but it will always act in a levelling way, parts of the image lying near the edge receiving more diffused radiation from the middle parts of the disk, than receive the central parts of the image from the marginal parts of the disk.

We may completely avoid this source of error by using a method in which the radiating power of the different parts of the disk is calculated from observations made on the occasion of a total eclipse of the Sun.

Let us suppose the curve, representing the intensity of the solar radiation from the first until the fourth contact as a function of time, to be exactly known²⁾. The curve will show us by how much the total radiation has increased or decreased between any two epochs. Every (positive or negative) increment is exclusively due to rays coming from that strip of the solar disk through which the Moon's limb has appeared to move between those very epochs.

Suppose the time after third contact to be divided into equal intervals of, say, 2 minutes, and the position of the Moon's limb at the end of each interval delineated on the solar disk, then the latter will be divided into 39 narrow strips, successively contributing the *known* quantities a, b, c, d, \dots to the total radiation.

Now, let us distinguish n concentric zones on the solar disk and denote by $x_\alpha, x_\beta, \dots, x_n$ the radiation coming from these zones per

¹⁾ Cf. J. SCHREINER, *Strahlung und Temperatur der Sonne*, p. 43—49 (1899).

²⁾ It is well known that, at Burgos, the observation of the eclipse of August 30, 1905, has not been favoured with a clear sky (Cf. the Preliminary Report in the Proceedings of the Meeting of November 25, 1905). Nevertheless, the measurements of total radiation have yielded some results of sufficient accuracy to justify that, in our present investigation, we make use of the radiation curve then secured. Further particulars regarding the observations will soon be published in the complete report on our expedition.

unit surface: (According to results obtained by LANGLEY and by FROST we shall suppose the radiating power to vary only with the distance from the center, not with the position angle). One of the strips will contribute to the radiation :

$$d = \sigma_1 x_\alpha + \sigma_2 x_\beta + \dots \sigma_n x_\nu,$$

if it cuts out of the first zone an area σ_1 , out of the second zone an area σ_2 , etc. The next strip contributes :

$$e = \varepsilon_1 x_\alpha + \varepsilon_2 x_\beta + \dots \varepsilon_n x_\nu,$$

and so on. We get 39 equations from which $x_\alpha, x_\beta, \dots x_\nu$ may be resolved.

Determination of the coefficients of the n unknown quantities.

I have found the coefficients $\sigma_1, \sigma_2, \dots \varepsilon_1, \varepsilon_2, \dots$ by weighing. On a piece of excellent homogeneous paper the solar disk was drawn and divided into a suitable number of concentric zones, which were intersected by arcs representing the Moon's limb in its successive positions. The following astronomical data, necessary for making the drawing, have been kindly procured to me by prof. A. A. NIJLAND.

contact	I	II	III	IV
position angle	293°,4	104°,5	304°,9	114°,9
local time	23 ^h 33 ^m 10 ^s	0 ^h 51 ^m 58 ^s	0 ^h 55 ^m 39 ^s	2 ^h 12 ^m 14 ^s

Moon's radius : Sun's radius = 132,8 : 126,8.

Now the strips were carefully separated from each other and weighed (for subsequent control). Then each strip was cut along the zone circles, and the pieces were weighed separately. In order to make the pieces recognizable, the zones had all been differently painted, each with a narrow line of water-colour. The weighings, which were accurate to half a milligram, gave the coefficients of the unknown quantities $x_\alpha, x_\beta, \dots x_\nu$. So the unit of area, adopted for measuring the surface of the solar disk, corresponds to a piece of our drawing paper weighing 1 milligram.

The breadth of each of the outer five concentric zones was $\frac{1}{10}$ of the Sun's radius; then came seven zones with breadth $\frac{1}{10}$ of the radius each, leaving round the center a circle with radius $\frac{1}{10}$. The average distances of the zones from the center, expressed in thousandth parts of the radius, will now be used as indices α, β, \dots of our 13 unknown quantities; so these will be written :

$$x_{975}, x_{925}, x_{875}, x_{825}, x_{775}, x_{700}, x_{600}, x_{500}, x_{400}, x_{300}, x_{200}, x_{100}, x_0.$$

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$$\begin{aligned}
a &= 126 x_{77} \\
b &= 66 x_{77} + 101 x_{99} \\
c &= 28 x_{77} + 59 x_{99} + 84 x_{87} + 1 x_{99} \\
d &= 18 x_{77} + 29 x_{99} + 50,5 x_{87} + 77 x_{99} + 1,5 x_{77} \\
e &= 13 x_{77} + 19 x_{99} + 27,5 x_{87} + 46 x_{99} + 69,5 x_{77} + 2 x_{70} \\
f &= 10 x_{77} + 14 x_{99} + 19 x_{87} + 28 x_{99} + 40 x_{77} + 66 x_{70} \\
g &= \\
h &= 8 x_{77} + 10 x_{99} + 12 x_{87} + 15 x_{99} + 18 x_{77} + 57 x_{70} + 58 x_{90} \\
i &= \\
j &= 7 x_{77} + 8 x_{99} + 9 x_{87} + 10,5 x_{99} + 12,5 x_{77} + 30 x_{70} + 48 x_{90} + 51 x_{90} \\
k &= \\
l &= 6 x_{77} + 6,5 x_{99} + 7 x_{87} + 8 x_{99} + 9 x_{77} + 23 x_{70} + 28,5 x_{90} + 40 x_{90} + 45 x_{90} \\
m &= \\
n &= 5,5 x_{77} + 6 x_{99} + 7 x_{87} + 8 x_{99} + 8 x_{77} + 19 x_{70} + 21 x_{90} + 25 x_{90} + 33 x_{90} + 36 x_{90} \\
o &= \\
p &= 5,5 x_{77} + 6 x_{99} + 6,5 x_{87} + 7 x_{99} + 7 x_{77} + 16 x_{70} + 17,5 x_{90} + 19,5 x_{90} + 22,5 x_{90} + 26,5 x_{90} + 31 x_{90} \\
q &= \\
r &= 5,5 x_{77} + 6 x_{99} + 6,5 x_{87} + 7 x_{99} + 7 x_{77} + 15,5 x_{70} + 16,5 x_{90} + 17,5 x_{90} + 18,5 x_{90} + 21,5 x_{90} + 20,5 x_{90} \\
s &= 5,5 x_{77} + 6 x_{99} + 6,5 x_{87} + 7 x_{99} + 7 x_{77} + 15 x_{70} + 15,5 x_{90} + 16,5 x_{90} + 17 x_{90} + 17,5 x_{90} + 18 x_{90} + 19 x_{90} + 8 x_{90}
\end{aligned}$$

On p. 670 the equations are written out. We have confined ourselves to 13 equations; increasing this number would not have led to greater accuracy, as the values of $a, b, c \dots$ had to be found from the radiation curve, that is by graphical interpolation, in which process it is understood that *all* of the observations have already been taken into consideration.

Determination of the constant terms of the equations.

Table I contains the results of the observations made at Burgos with our actinometer. The second column gives the galvanometer deflections, from which the numbers of the third column, representing the intensity of the radiation, are calculated ¹⁾.

Owing to the clouds there are large gaps in the series of observations; but nevertheless, after the results had been plotted down, we saw that there was only little room left for fancy when drawing the radiation curve in such a way, that closest agreement with the observational data was obtained. As a matter of course the curve has not been drawn *between the series of points*, but *so as to join the highest points*, for the observed values could only be too small. Only one exception is made to this rule, the value found at 0^h 17^m 3^s being very probably too high by some error or instrumental disturbance.

The middle part of the radiation curve has been reproduced on the annexed plate. For determining a, b, c, \dots we have used the part included between 0^h 55^m and 1^h 37^m, which was very carefully constructed on a larger scale. It deserves notice that the relative accuracy of the small ordinates (corresponding to few minutes after totality) is nearly as great as that of the larger ones, because the galvanometer deflections from which they were calculated are all lying between 118 and 347 scale divisions. Table II refers to this part of the radiation curve. In the second column are given the ordinates of the curve at the epochs 0^h 55^m 40^s and every two minutes later; the unit corresponds to an intensity = 1000.

1) Particulars concerning the connection between the numbers of these two columns will be found in the forthcoming report on the Dutch expedition. The method and the instruments used at Burgos were the same that are described in: "Total Eclipse of the Sun, May 18, 1901. Reports on the Dutch Expedition to Karang Sago, Sumatra, N°. 4: Heat Radiation of the Sun during the Eclipse", by W. H. JULIUS. The numbers of the third column are proportional to the total radiation coming from a circular patch of the sky, 3° in diameter, with the Sun in its center.

T A B L E I.

Time.	Galvano- meter- deflections.	Intensity of radiation.	Time.	Galvano- meter- deflections.	Intensity of radiation.
22 ^h 28 ^m 48 ^s	280	1750000	0 ^h 20 ^m 48 ^s	128.5	819000
36 0	231	1444000	2nd contact 51 58		
38 33	287	1794000	53 53	3	9
			54 28	13	13
46 58	287	1794000	55 18	33	33
51 38	270	1688000	3rd contact 55 40		
53 49	260.5	1631000	55 58	600?	600?
56 8	278.5	1745000	57 58	118.5	23000
			58 33	98.5	19100
23 4 58	256	1610000	59 13	219.5	42700
8 3	283.5	1786000	59 53	286	55700
9 56	284.5	1792000	1 1 18	232.5	74800
11 44	275	1736000	2 28	170	108800
1st contact 33 8			3 3	152.5	97700
35 48	226	1430000			
38 3	256.5	1625000	7 38	323.5	207000
40 38	269.5	1709000			
41 38	270	1712000	21 15	331.5	635000
42 48	270.5	1715000	22 3	347.5	665000
44 0	260	1649000	23 3	151.5	676000
45 33	259.5	1646000	23 58	162	722000
46 38	256.5	1627000	24 53	167	745000
47 52	248.5	1566000	25 53	174	776000
48 53	250.5	1589000	26 53	180.5	805000
50 8	249	1580000	27 53	186.5	832000
51 33	241	1529000	28 58	194	865000
53 8	233.5	1483000	30 8	201	897000
55 3	227	1442000	31 8	207.5	926000
56 33	226	1435000	32 11	213	950000
58 23	216.5	1376000	33 13	220	981000
			34 20	225.5	1007000
0 7 23	192	1222000	35 25	232.5	1037000
8 53	184	1170000	36 34	237.5	1060000
10 28	177	1127000			
11 43	171.5	1091000	2 1 58	338	1506000
13 13	165.5	1054000	3 8	248	1581000
14 58	159	1013000	4th contact 12 24		
17 3	150	956000	13 18	258.5	1648000
19 28	136	867000	14 20	260	1657000

But this observational curve has to be corrected, owing to the circumstance that in the lapse of time considered the Sun's altitude has diminished. We may proceed as follows. Apart from a possible influence of sun-spots or faculae there is no reason why the eclipse curve would not be symmetrical if the Sun's altitude (and the condition of our atmosphere) remained constant. Between 23^h and 1^h the variation of altitude is very small. Now taking 0^h 53^m 50^s as

TABLE II.

Time	Ordinates of radiation curve.	Ordinates of corrected radiation curve.	Increments
u m s 0 55 40	0	0	
57 40	20.1	20.1	20.1 = a
59 40	52.5	52.5	32.4 = b
1 1 40	91.0	91.0	38.5 = c
3 40	136.5	136.5	45.5 = d
5 40	187	187	50.5 = e
7 40	240	241	54 = f
9 40	296	297	56 = g
11 40	354	355	58 = h
13 40	412	414	59 = i
15 40	472	474	60 = j
17 40	532	535	61 = k
19 40	594	597	62 = l
21 40	655	659	62 = m
23 40	717	721	62 = n
25 40	776	783	62 = o
27 40	834.5	844.5	61.5 = p
29 40	891.5	905.5	61 = q
31 40	947	966	60.5 = r
33 40	1001	1026	60 = s
35 40	1053.5	1085.5	59.5 = t

TABLE III.

Radiation per unit surface of the concentric zones of the solar disk.
$x_{975} = 0.1595$
$x_{945} = 0.2166$
$x_{915} = 0.2501$
$x_{885} = 0.3023$
$x_{855} = 0.3290$
$x_{825} = 0.3488$
$x_{795} = 0.3662$
$x_{765} = 0.3843$
$x_{735} = 0.4153$
$x_{705} = 0.4278$
$x_{675} = 0.4240$
$x_{645} = 0.4380$
$x_{615} = 0.4388$

the epoch of mid-eclipse, we draw a horizontal line through a point m corresponding to that epoch. The line cuts the descending branch of the curve in l ; we make $mn = ml$ and thus find a point n of the hypothetical radiation curve for constant altitude of the Sun. Acting in a similar way for a few more points, we get an idea of the magnitude of the smoothly increasing correction which is to be applied to the ordinates of the ascending branch. K. ÅNGSTRÖM's measures of the intensity of the radiation for different altitudes of the Sun¹⁾ have also been considered in determining the correction.

The third column of Table II contains the ordinates of the corrected curve; in the fourth column are given their successive increments which, of course, are the values to be assigned to the absolute terms of our equations.

Results.

The solution of the equations leads to the numbers of Table III; the results are plotted down in fig. 2 on the plate. Through these points we have drawn a curve satisfying the condition that its curvature should gradually diminish; it shows us the law of variation of the radiating power from the edge toward the center of the solar disk. Putting the ordinate at the center equal to 100 and expressing the other ordinates in the same unit, we get numbers comparable with the results obtained by other investigators.

The comparison with the spectro-photometric observations by H. C. VOGEL²⁾ and with the measurements of total radiation made with a radio-micrometer by WILSON³⁾ and with a thermopile by FROST⁴⁾, is given in Table IV. We add in Table V the results of a spectro-bolometric investigation by VERY⁵⁾, as these numbers have been used by VERY and by SCHUSTER⁶⁾ in testing their explanations of the phenomenon.

According to FROST's measurements the total radiation appears to diminish from the center toward the limb in about the same proportion as the radiation of wave-length $650\mu\mu$, whereas my numbers show a decrease very similar to that exhibited by rays of wave-

1) K. ÅNGSTRÖM, Intensité de la radiation solaire à différentes altitudes. Recherches faites à Ténériffe 1895 et 1896.

2) H. C. VOGEL, Ber. d. Berl. Akad. 1877, p. 104.

3) W. E. WILSON, Proc. Roy. Irish Acad. [3], Vol. 2, p. 299, (1892).

4) E. B. FROST, Astron. Nachr. 130 (1892), p. 129.

5) F. W. VERY, Astroph. Journ. 16 (1902), p. 73.

6) A. SCHUSTER, Astroph. Journ. 16 (1902), p. 320; 21 (1905), p. 258.

T A B L E IV.

Distance from center of disk.	H. C. VOGEL's spectro-photometric measurements.						Total radiation.		
	405—412	440—446	467—473	510—515	573—585	658—666	Receiver in solar image.		Eclipse-curve.
	$\mu\mu$	$\mu\mu$	$\mu\mu$	$\mu\mu$	$\mu\mu$	$\mu\mu$	WILSON	FROST	JULIUS
0.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
0.1	99.6	99.7	99.7	99.7	99.8	99.9	99.9	99.9	99.8
0.2	98.5	98.7	98.8	98.7	99.2	99.5	99.6	99.4	98.6
0.3	96.3	96.8	97.2	96.9	98.2	98.9	98.8	98.4	96.6
0.4	93.4	94.1	94.7	94.3	96.7	98.0	97.3	96.3	94.0
0.5	88.7	90.2	91.3	90.7	94.5	96.7	95.3	93.6	90.3
0.6	82.4	84.9	87.0	86.2	90.9	94.8	92.5	89.8	85.5
0.7	74.4	77.8	80.8	80.0	84.5	91.0	88.7	84.6	79.5
0.75	69.4	73.0	76.7	75.9	80.1	88.1			75.3
0.8	63.7	67.0	71.7	70.9	74.6	84.3	83.9	77.9	70.1
0.85	56.7	59.6	65.5	64.7	67.7	79.0			63.5
0.9	47.7	50.2	57.6	56.6	59.0	71.0	74.9	68.0	55.0
0.95	34.7	35.0	45.6	44.0	46.0	58.0		(60.5)	44.0
1.0	13.0	14.0	16.0	16.0	25.0	30.0	45.1		(24.0)

T A B L E V.

Distance from center.	F. W. VERY's spectro-bolometric measurements.						
	416 $\mu\mu$	468 $\mu\mu$	550 $\mu\mu$	615 $\mu\mu$	781 $\mu\mu$	1010 $\mu\mu$	1500 $\mu\mu$
0.5	85.8	90.2	93.3	94.8	94.1	94.3	95.9
0.75	74.4	76.4	83.1	84.5	88.5	89.4	95.0
0.95	47.1	46.2	58.7	68.1	74.9	76.5	85.6

length 510 $\mu\mu$. At first sight the evidence is in favour of the results obtained by FROST, because the maximum of the curve representing the energy in the solar spectrum (or perhaps rather the "center of gravity" of the enclosed surface) lies closer to 650 $\mu\mu$ than to 510 $\mu\mu$. But this argument fails; for the measurements of VOGEL and those of FROST are all disturbed alike by atmospheric diffusion. Had the spectro-photometric observations been free from this influence, then the rate of decrease of the radiation from the center toward the

limb would doubtless have been found quicker for all wave-lengths, and, very probably, the distribution for the region 650μ would have proved to agree better with my results than with the uncorrected values of FROST.

WILSON'S measurements seem to have been influenced by other causes of error still, besides atmospheric scattering, as his numbers are greater than those obtained by FROST, and harmonize not as well as the latter with the spectro-photometric series.

The observations of VERY have given considerably greater ratios in the marginal regions than those of VOGEL. Mr. VERY himself points out the difference, and remarks that the bolometer has an advantage over the eye in the red where the heat is great; but I may suggest, on the other hand, that instrumental errors (reflection or scattering of light by prisms, lenses, tubes, etc.) are easier discovered and corrected in spectro-photometric than in spectro-bolometric work.

It seems to me that observing an eclipse-curve by means of a very simple but sensitive actinometer, without lenses or mirrors, must yield results concerning the radiation of different parts of the solar disk which deserve more confidence than the values hitherto obtained in other ways. I wish to lay stress upon the advantages of our *method*, rather than on the reliability of the numbers secured at Burgos under not very favourable circumstances. In a clear sky the shape of the eclipse curve will easily be found with very great accuracy.

The same method will also be applicable with radiations covering limited parts of the spectrum, if we only put suitable ray-filters before the opening of one of the diaphragms in the actinometer. It may even be possible, in a future eclipse, to use an arrangement which brings several ray-filters by turns before the opening; thus, when disposing of a quick galvanometer, one would be able to simultaneously determine, with one actinometer, the eclipse curves for rays belonging to five or more regions of the spectrum, and the results would be independent of selective atmospheric scattering.

Remarks on the hypotheses used for explaining the distribution of the radiating power on the solar disk.

The diminution of the intensity of radiation toward the limb is almost generally ascribed to absorption of the rays by the solar atmosphere¹⁾, and it is supposed that, in absence of that atmosphere,

¹⁾ J. SCHEINER goes as far as to say: "Eine andere Deutung des Lichtabfalls ist nicht zulässig." (Strahlung und Temperatur der Sonne, p. 40).

the photosphere would show itself as an equally luminous disk. But then it appears to be impossible to find such values for the thickness of that atmosphere and for its coefficient of absorption, as to give a law for the rate of diminution of brightness, consistent with observation. VERY ¹⁾ e.g. when attributing the effect to absorption only, arrives at the absurd result that we should have to assume that the absorptive power toward the limb is smaller than that nearer the center. He, therefore, suggests the existence of other influences which, combining with the absorbent process, would reconcile theory to observed facts. Diffraction by fine particles, columnar structure of the solar atmosphere, irregularity of the photospheric surface, are thus introduced.

SCHUSTER ²⁾, on the other hand, is of opinion that the difficulty which has been felt in explaining the law of variation of intensity across the solar disk is easily removed by placing the absorbing layer sufficiently near the photosphere and taking account of the radiation which this layer, owing to its high temperature, must itself emit. He then really finds values for the absorption and the emission of that layer, harmonizing with the results of VERY's and WILSON's ³⁾ measurements, and also with the properties of the energy curve of the spectrum of a black body at different temperatures. But, for all that, serious doubts as to the correctness of the premise and the conclusions must subsist.

Indeed, the calculations of SCHUSTER as well as those of VERY, WILSON, LANGLEY, PICKERING and others, concerning the same subject, are based on the assumption that the light travels along straight lines through the solar gases, whereas everybody who has duly noticed A. SCHMIDT's "Strahlenbrechung auf der Sonne" will at the least have to give in that rays coming from the outer zones of the disk must have followed curved paths through the solar atmosphere. By this circumstance the said calculations lose their convincing power.

And besides, the fundamental idea that a considerable portion of the photospheric radiation should be absorbed by a thin atmosphere, encounters a difficulty of greater importance still. This point, I think, has also first been moved by A. SCHMIDT. What becomes of the absorbed energy accumulating in the atmosphere? According to SCHUSTER e.g. (l.c. p. 322) the atmosphere transmits largely $\frac{1}{2}$, of

¹⁾ F. W. VERY. The absorptive power of the solar atmosphere. *Astroph. Journ.* 16, p. 73—91; (1902).

²⁾ A. SCHUSTER. *Astroph. Journ.* 16, p. 320—327, (1902); 21, p. 258—261, (1905).

³⁾ W. E. WILSON and A. A. RAMBAUT. *Proc. Roy. Irish Acad.* [3], 2, p. 299—334, (1892).

the radiation emitted by the photosphere ; so it stops almost $\frac{1}{2}$, and only a small fraction of this absorbed energy leaves the Sun in the form of radiation, emitted by the atmosphere itself. After all, more than half of the radiation coming from the photosphere is retained by the absorbing layer, and we cannot suppose it to go back to the interior without violating the second law of thermodynamics. As long as it has not been shown how the solar atmosphere may get rid of that immense quantity of energy continually supplied and never radiated, similar considerations will remain very unsatisfactory.

Our problem appears to be much less intricate when viewed from the stand-point taken by SCHMIDT ¹⁾, though the mathematical treatment will not be easy. A uniformly luminous sphere surrounded by a concentric, perfectly transparent refracting envelope, will offer the aspect of a disk the brightness of which diminishes towards the limb. This has been established approximately by SCHMIDT for the case of a homogeneous, sharply limited envelope. It is easily understood that a similar result must be obtained when assuming a transparent atmosphere of gradually decreasing density and refractive power ; but then, of course, the rate at which the luminosity varies on the disk will depend on the law of density variation. We may proceed a little farther, and accept SCHMIDT's hypothesis that the incandescent core of the Sun is *not* a sphere with a sharp boundary, but a gaseous body the density and radiating power of which are smoothly diminishing along the radius. In this way, I think, we dispose of premises from which it seems possible to derive an explanation of the general aspect of the solar disk without involving into such serious difficulties as were hitherto encountered.

Chemistry. — "*On the nitration of ortho- and metadibromobenzene.*"

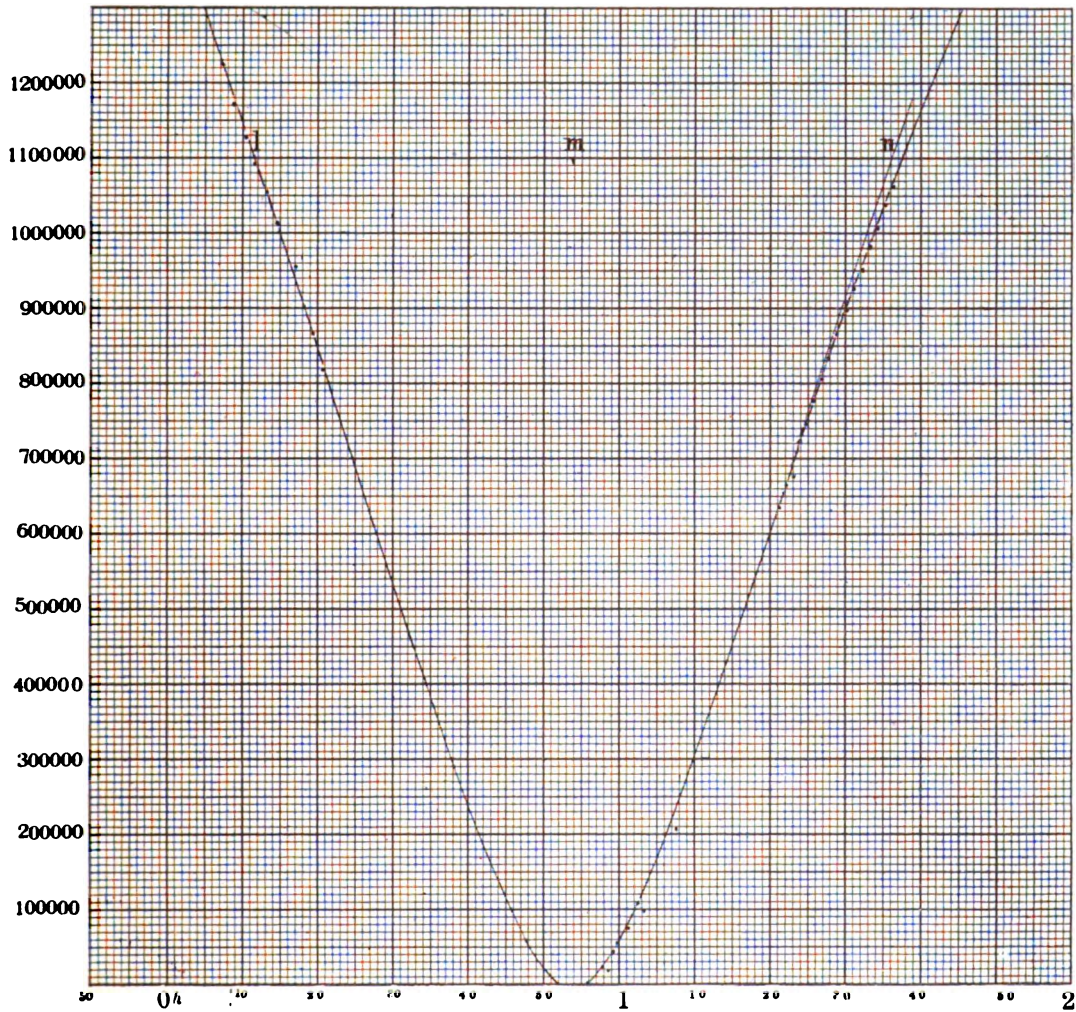
By Prof. A. F. HOLLEMAN.

(Communicated in the meeting of January 27, 1906).

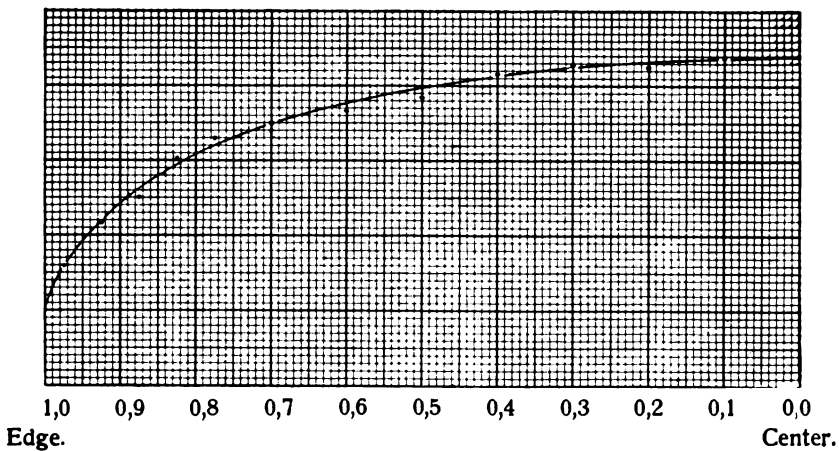
After the disturbing influence which the halogen atoms exercise on each other's directing influence in regard to the nitro-group, had been noticed in the nitration of the dichlorobenzenes, it was necessary to extend this research to the nitration of the dibromobenzenes so as to be able to find the connection between the results with the dichloro- and dibromocompounds and to compare the same with the result of the nitration of the corresponding monohalogen benzenes.

¹⁾ A. SCHMIDT, Physik. Zeitschr. 4, 282, 341, 453, 476 ; 5, 67, 528. (1903 and 1904).

Middle part of the radiation curve obtained during the solar eclipse of August 30, 1905.



Radiating power across the solar disk.



Edge.

Center.

The necessary experiments have been considerably delayed, because it appeared that the ortho- and meta-dibromobenzenes had not as yet been obtained in a perfectly pure condition, and the search for a good method absorbed much time. We have at last succeeded in preparing *m*-dibromobenzene from perfectly pure *m*-bromoaniline by diazotation in a dilute hydrobromic acid solution, according to a direction given by ERDMANN for another purpose. *Meta*-dibromobenzene has a sp. gr. of 1.960 at 18.5°, and solidifies at — 7°. It is true that F. SCHIFF incidentally mentions (M. 11, 335) that he has met with *m*-dibromobenzene solidifying at + 1°, without saying how he has obtained the same, but there is good reason for doubting the correctness of this statement. In this case, the product obtained by me and my coadjutors (SIRKS, SLUITER) with its 8° lower solidifying point should contain about 16% of impurities. In the nitration of our *m*-dibromobenzene, however, a product is obtained having a sp. gr. such as was to be expected from a mixture of the isomers ($\text{Br}^1 : \text{Br}^3 : \text{NO}_2^4$) and ($\text{Br}^1 : \text{Br}^3 : \text{NO}_2^3$) brought together in the proportion indicated by the solidifying point, so that a contamination of our preparation with such a large quantity of another substance is altogether out of the question; moreover, on distillation our preparation yielded two fractions within one degree which both possessed practically the same sp. gr. and solidifying point.

O-dibromobenzene which was obtained in an analogous manner from *o*-bromoaniline, had a sp. gr. of 1.996 at 11° and solidified at + 6°.

The preparation of the six dibromonitrobenzenes was carried out in a manner analogous to that of the six dichloronitrobenzenes, described by me in the "Recueil" 23, 357.

The composition of the products of nitration of the dibromobenzenes was determined from their solidifying point and their sp. gr. and led to the results united in the subjoined table with the composition of the products of nitration of the dichlorobenzenes. The temperature of the nitration was 0°. (See p. 680).

In ortho-dibromobenzene the disturbance of the directing power of the one halogen atom owing to the presence of the other one is, therefore, much less than in the case of orthodichlorobenzene because in the first one 18.3 and in the second only 7.2% of by-product is formed, whilst monobromo- and monochlorobenzene yield, respectively, 29.8 and 37.6% of by-product. On the other hand, the disturbance caused by the entry of the nitro-group between the two halogen atoms in *m*-dibromobenzene is very nearly equal to that in *m*-dichlorobenzene, therefore much larger in regard to the ortho-

	Quantity of by-product in %	Quantity of by-prod. in 100 parts of main prod.
<i>o</i> -C ₆ H ₄ Cl ₂	7.2	7.8
<i>m</i> -C ₆ H ₄ Cl ₂	4.0	4.1
<i>o</i> -C ₆ H ₄ Br ₂	18.3	22.4
<i>m</i> -C ₆ H ₄ Br ₂	4.6	4.8
C ₆ H ₅ Cl	29.8	42.0
C ₆ H ₅ Br	37.6	60.5

compounds. One would feel inclined to attribute this to "steric disturbances" introduced into Organic Chemistry by V. MELJER, were it not that the specific volume of chlorine and of bromine in the dichloro- and dibromobenzenes differs but little.

Perhaps it is rather the atomic weight of chlorine and bromine which has some connection with the above. For further particulars concerning this research the "Recueil" should be consulted.

Amsterdam, Org. chem. Lab. of the University, January 1906.

Chemistry. — "*The introduction of halogen atoms into the benzene core in the reduction of aromatic nitro-compounds*". By Dr. J. J. BLANKSMA. (Communicated by Prof. A. F. HOLLEMAN).

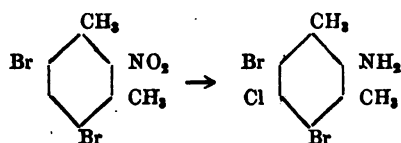
(Communicated in the meeting of January 27, 1906).

Some time ago I cited and communicated some experiments¹⁾ which showed that, in some cases, in the reduction of aromatic nitrocompounds, halogen atoms may be removed from the benzene core. In 1901 an article by PINNOW²⁾ appeared in which a fairly large number of cases are mentioned, where halogen atoms are introduced into the benzene core in the reduction of aromatic nitrocompounds. PINNOW endeavours to find the conditions under which this secondary reaction is as much as possible prevented in order to prevent formation of halogenised amidocompounds as by-products, alongside the amidocompounds.

¹⁾ Proc. 30 March 1904, Recueil 24, 320.

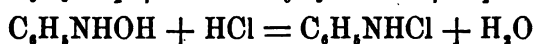
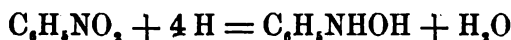
²⁾ Journ. für Prakt. Chem. (2) 63, 352.

So when I obtained 5-chloro-4,6-dibromo-2-amido-*m*-xylene as by-product in the reduction of 4,6-dibromo-2-nitro-*m*-xylene, I tried to



introduce halogen atoms into the core, taking the simplest case, namely, the reduction of nitrobenzene with tin and hydrochloric acid.

As is well-known, various intermediate products are formed in the reduction of nitrobenzene to aniline. The formation of chloroaniline from nitrobenzene may be explained in the following manner:¹⁾



The fact that, in the reduction of nitrobenzene, phenylhydroxylamine occurs as an intermediate compound, has been demonstrated by BAMBERGER, who has also proved that, on boiling phenylhydroxylamine with hydrochloric acid, *o*- and *p*-chloroaniline are formed²⁾. It has also been proved by LÖB that *o*- and *p*-chloroanilines are formed in the electrolytic reduction of nitrobenzene in alcoholic hydrochloric acid solution³⁾. The object of the experiments to be described was to try and conduct the reduction of nitrobenzene with tin and hydrochloric acid in such a manner that instead of aniline, as much as possible chloroaniline was formed.

The experiment had, therefore, to be carried out in such a way, that the phenylhydroxylamine formed was not at once further reduced to aniline, but to give this substance an opportunity to be converted into chloroaniline, under the influence of hydrochloric acid. The conditions were also to be such that the phenylchloroamine $\text{C}_6\text{H}_5\text{NHCl}$, which is formed intermediary, could be readily converted into chloroaniline.

The intramolecular conversion of phenylchloroamine into *o*- and *p*-chloroaniline is, however, but little known, as the first substance is very unstable but the conditions under which acetylchloroanilide is converted into *p*-chloroacetanilide have been closely investigated. It has been shown that this reaction is very much accelerated by increase of the temperature and also by addition of hydrochloric acid⁴⁾.

¹⁾ LÖB, Die Electrochemie der Organischen Verbindungen p. 166, 3e Auflage (1905).

²⁾ Ber. 28, 451. BAMBERGER and LAGUTT, Ber. 31, 1503.

³⁾ Ber. 29, 1896.

⁴⁾ BENDER, Ber. 19, 2273. BLANKSMA, Recueil 21, 366, 22, 290.

If, on account of the analogy between phenyl-chloroamine and acetylchlorophenylamine, we assume that in the case of the first substance the velocity of the conversion into *o*- and *p*-chloroaniline is also strongly accelerated by elevation of temperature and addition of hydrochloric acid, the conditions for obtaining chloroaniline instead of aniline, in the reduction of nitrobenzene with tin and hydrochloric acid, are as follows:

1. Slow reduction, or addition of tin in small quantities at the time, in order not to at once reduce the phenylhydroxylamine to aniline.
2. Excess of hydrochloric acid so as to rapidly convert the phenyl-chloroamine formed into chloroaniline.
3. The reaction should take place at the boiling temperature, as elevation of temperature also promotes this conversion.

The experiment was now conducted as follows:

10 cc. of nitrobenzene were dissolved in 100 cc. of alcohol and 200 cc. of 25 % hydrochloric acid were added. This solution was boiled over the naked flame, whilst 15 grams of tin were added through the reflux condenser in small portions. Each time, after adding a small amount of tin, the boiling was continued until everything had dissolved before adding a fresh portion. The experiment lasted six hours. The unaltered nitrobenzene was now removed by steam, the residue was rendered alkaline and the aniline and chloroaniline recovered by distillation in steam.

In this way, 6.5 gram of oil were obtained. The greater portion of this oil was distilled between 182° and 225°, the residue solidified in the distilling flask, and proved to be *p*-chloroaniline (m. p. 70°). The oil consisted of aniline and *o*- and *p*-chloroaniline.

From a chlorine determination according to Carius, it appeared that the mixture consisted of 55% of chloroaniline and 45% of aniline.

If the reduction experiment was made with SnCl_2 and HCl (*o*+*p*) chloroaniline (53%) were formed together with aniline. In this case, the stannous chloride was also added in small portions, so as to give the intermediary formed phenylhydroxylamine an opportunity of being converted into *o*- and *p*-chloroaniline. Nitroso-benzene gives the same result ¹⁾.

In the same manner, the reduction of nitrobenzene with tin and hydrobromic gave a mixture of aniline and (*o*- and *p*)-bromoaniline.

At present it is still difficult to predict which aromatic nitro-

¹⁾ Cf. GOLDSCHMIDT, Zeitschrift für Phys. Chem. 48, 435.

compounds will yield a large quantity of halogenised by-products on reduction with tin and hydrochloric acid. It would be necessary to know something more about the reduction velocity of the nitrocompounds ¹⁾ (and of the intermediary formed hydroxylaminoderivatives), and about the intramolecular conversion velocities of the halogenphenylamines.

It is known, for instance, that *o*-nitrotoluene gives a large amount of chlorinated by-product on reduction with tin and hydrochloric acid ²⁾. The *o*-tolylhydroxylamine formed as intermediate product is, therefore converted here into 5-chlorotoluidine, and the reduction experiments of GOLDSCHMIDT ³⁾ on *o*-nitrotoluene are in agreement with this. GOLDSCHMIDT has shown that, with increase of the temperature the reduction velocity also increases, whilst an elevation of temperature also increases the conversion velocity of the halogenphenylamines. It now appears that this last reaction is the most strongly accelerated, for the amount of halogenised by-products increases with elevation of the temperature ⁴⁾.

Resumé. It has been shown that the reduction of nitrobenzene with tin (or Sn Cl₂) and hydrochloric acid may be carried out in such a manner that *p*-chloroaniline occurs as the main product. The cause of this must be explained by the fact that, in the reduction of nitrobenzene, phenylhydroxylamine occurs as an intermediate product. As on reduction of all aromatic nitrocompounds, hydroxylamine derivatives are formed as intermediate compounds, we shall generally notice on reduction of such nitrocompounds with tin and hydrochloric acid, besides amidocompounds, also halogenised amidocompounds (with halogen atoms *o*- or *p*- in regard to the NH₂ group), whilst the quantity of these two last substances will be dependent on the conditions under which the reduction is carried out. In some cases no halogen atoms are introduced, but they are even eliminated from the benzene core ⁵⁾.

I hope to record more fully further experiments in the *Recueil* later on.

Amsterdam, January 1906.

¹⁾ See the note on the preceeding page.

²⁾ BEILSTEIN and KÜHLBERG, *Ann*, 156, 81. HOLLEMAN and JUNGUS, *Chemisch Weekblad* II. 558.

³⁾ l. c.

⁴⁾ PINNOW, l. c.

⁵⁾ *Recueil* 24, 320.

Botany. — “*On a case of apogamy observed with *Dasyllirion acrotrichum* Zucc.*” By Prof. F. A. F. C. WENT and A. H. BLAAUW.

In the summer of 1904 a specimen of *Dasyllirion acrotrichum* Zucc. was in bloom in the Utrecht Botanical Garden. The home of this tree-like Liliacea is in Mexico; on a short stem it bears a bundle of flat leaves with thorny margins. Although the plant is pretty often cultivated in European botanical gardens it is very seldom seen in bloom. Hence constant attention was paid to the here mentioned specimen. The inflorescence was two metres long; the principal axis was ramified and had a great number of steeply erected lateral axes in the axils of bracts; each of these carried some 50 to 150 unstalked female flowers. *Dasyllirion* is dioecious so that male flowers were entirely absent.

Each flower had a perianth consisting of six green leaflets and a pistil; this latter consisted of a triangular ovary with a short style and three stigmas. The ovary was unilocular and had on its bottom three ovules.

After the flowers had finished blooming it seemed as if some ovaries began to swell. As there could be no question of fertilisation in the absence of male sexual organs, it was thought that perhaps a new case of apogamy or parthenogenesis was present here. The ovaries were now regularly examined; they more and more assumed the appearance of little fruits, looked like small nuts provided with three wings and strongly reminded one of the fruitlets of *Rheum*. It appeared that many ovules swelled, but never more than one in each ovary. Not nearly in all flowers this phenomenon was observed, in no more than 10 to 40 percent it was at all visible.

For a detailed investigation these ovules were now fixed in FLEMMING's fixing solution (the weak solution) and then washed in the usual manner and gradually placed in strong alcohol. This was done for the first time on August 15; from 158 ovaries 49 ovules were obtained, i.e. 31 percent. This was a maximum, however, for when later material was collected in the same way on August 22, September 3, 10, 13, 19 and 25, October 8 and 22, November 12, December 15 and 24 and on January 19, 1905, each time more and more ovules appeared to be unfit for use, as they began to wrinkle. Such as looked more or less swollen were fixed; among these some had grown thicker and finally the impression was that some seeds had ripened. But ultimately not a single germinable seed appeared to be on the plant and after January 19 no material fit for investi-

gation could be got. Notwithstanding this the preserved material was examined, since it was possible that only the unfavourable conditions under which *Dasyllirion* lived in the Botanical Garden at Utrecht, were the reason why no ripe seed was formed.

On microscopical examination phenomena were indeed observed which seemed to point to apogamy or parthenogenesis, but the material proved insufficient to obtain a consistent result. Leaving apart even the already mentioned fact that not a single ripe seed was produced, the number of ovules in which ultimately anything particular could be observed, was extremely small. For microscopic examination revealed that most ovules which outwardly showed nothing abnormal, were yet already in all stages of disorganisation.

Although we are unable to offer a finished investigation, yet it seemed desirable to us to publish what we have seen. For *Dasyllirion* blooms so seldom in Europe that for us the chance of finishing our investigation is practically nihil, while now at least attention has been drawn to it, so that perhaps in the mother country of the plant some one may feel inclined to re-examine it.

Moreover the number of known cases of apogamy or parthenogenesis is so small that there is every reason to publish each new case. And finally the material examined by us presents some points which deserve attention for special reasons.

The fixed material was embedded in paraffin, cut with the microtome and then stained, as a rule with saffranine only, sometimes with saffranine, gentian violet and orange G.

The ovules of *Dasyllirion* are anatropous and furnished with two integuments; the outer one consists, besides of an exterior and interior epiderm, of cells, situated rather irregularly in 2 to 4 rows; towards the chalaza it is much more strongly developed. The inner integument consists of two layers of closely adjacent cells. The micropyle is formed by the inner integument only, the edges of which are strongly swollen — the cells are larger and the thickness is here about four cells — and are closely adjacent, so that they only leave a narrow slit between them.

The tissue of the nucellus is small-celled near the chalaza, but for the rest it consists of large cells with very little protoplasm and apparently very much cell-sap. The more peripheral cells are smaller, their cell-walls are perpendicular to the integument, especially near the micropyle, but the others are greatly lengthened in the direction of the chalaza so that they have become tube-shaped. These tubes are often more or less bent, so that longitudinal sections present an appearance which is rather difficult to disentangle. The swelling of

the ovules was in many cases to be ascribed to the strong turgescence of these nucellus-cells only ; in older stages also the cells or the outer integument began to increase their volume, evidently also by the increase of the cell-sap only.

These strongly lengthened nucellus cells at first caused us to believe that more than one embryosac is formed, but an accurate examination of the preparations finally gave us the conviction that only one embryosac is found. Certainty on this point will be obtained only by investigating the development and for this purpose the collected material was unsuitable, for also in the youngest ovules the embryosac was already completely formed. It is long-drawn, somewhat in the shape of a dumb-bell, at the base extending near the chalaza, at the top near the micropyle surrounded by a single layer of nucellus cells.

Now it appeared that in the great majority of these embryosacs nothing particular could be observed ; sometimes a little protoplasm or more or less disorganised and swollen masses, but no egg-apparatus, no polar nuclei and no antipodal cells, so that presumably in nearly all the ovules a disorganisation had already taken place before they were fixed.

Only a few ovules presented more particularities and these we shall describe here, in the first place those where a young embryo was found.

In an ovule, collected on August 22, there is found at the top of the embryosac and filling this part of the latter entirely, a cellular body with eight normal looking nuclei, making the impression of an embryo. The rest of the embryosac is empty and only some disorganised masses lie in it ; of an endosperm nothing can be seen, no more than of antipodals or embryosac-nucleus ; concerning this latter, however, the possibility must be granted that it has fallen from the preparation during the staining, although we do not think this probable.

In an ovule, collected on September 10, the top of the embryosac is filled by a cell-mass of some 20 to 30 cells, the walls of which are strongly swollen ; the nuclei are small and are in a state of disorganisation as well as the rest of the protoplast. The whole makes the impression of a more or less disorganised embryo. Further there is in the embryosac a pretty large quantity of protoplasm in which we could find no nuclei.

Finally we found in an ovule, collected on August 22, a still larger cellular body, reminding us of an embryo. It consists of about 40 cells, the contents of which are still more disorganised, with swollen cell-walls which strongly absorb staining substances. Having regard to the former two preparations we are of opinion that this also

must be looked upon as an embryo, the development of which has already for some time been stopped and which is now in progress of disorganisation. Also here nothing peculiar was further found in the embryosac.

Of course we looked also for the presence of an egg-apparatus, especially in the younger stages, but there is only one preparation in which anything of this kind can be detected. It is an ovule, collected on August 22, where in the top of the embryosac three cells are found, two shorter ones with distinct nuclei and a third which is larger with disorganised cell-contents in which the nucleus can still be discovered, however. We believe this to be the egg, the others synergids. Here also nothing else is found in the embryosac except protoplasm, which stains strongly.

In 10 other ovules an endosperm was observed in various stages of development. It must be stated at once that in none of these anything of the nature of an embryo is seen. Although it may be objected that for some ovules the series of sections is not complete, yet this is certainly not the case with the majority. Especially where the micropyle is seen in the section, the embryo would be sure to be observed if it were there, but also in this case no trace of it can be found. So we arrive at the conclusion that here an endosperm has been formed without the embryo having developed.

An ovule, collected on August 15, shows the smallest quantity of endosperm. The upper part ($\frac{1}{4}$ to $\frac{3}{4}$) of the embryosac is filled up with it. The shape of the embryosac has been changed; it is swollen, has become cylindrical or somewhat broader towards the bottom, has a thickness of 0.4 mm., while the nucellus has a maximum diameter of 1.0 mm. The lower part of the embryosac in which no endosperm is found, has entirely collapsed and has evidently been squeezed by the surrounding cells. This same shape of the embryosac was met with only once without an endosperm having been formed in it, namely in an ovule, collected on the same day. In the lining protoplasmatic layer no nuclei could be seen, but still we believe that this was a first beginning of the formation of an endosperm. Now the endosperm of the just-mentioned ovule consists of thin-walled cells of varying size; normal nuclear divisions occur but also nuclei of abnormal size with a number of nucleoli, indicating fragmentation. At one of the sides of the embryosac the formation of the endosperm has not yet been completed.

Curiously enough the next stage in the development of the endosperm was observed with an ovule, fixed on December 15. Here the greater part of the tissue of the nucellus has been displaced, so that

it forms only a narrow layer round the endosperm, somewhat thicker near the chalaza (greatest thickness of the embryosac 1,2 mm., of the nucellus 1,5 mm.). Here also the lower part of the embryosac is not filled, but is entirely abortive. The endosperm-cells are of rather unequal size, most nuclei do not look normal, but still divisional stages occur; in the more peripheral cells small grains which strongly absorb staining substances appear outside the nucleus. As in some other cases, the impression is got here that the formation of the endosperm takes place rather irregularly, as if in various spots within the embryosac pieces of endosperm-tissue would form which grow towards each other so that seemingly more than one endosperm lies in the embryosac. At any rate this seems to be so when one limits his attention to one preparation; by comparing, however, the different successive sections of one ovule there finally appears to be only one mass of endosperm. The formation of the endosperm begins in the lining of the wall of the embryosac and from there proceeds inwardly; in this process the cavity is gradually filled up, the endosperm now meets itself from various sides and it is these divisional lines that remain visible.

That the formation of an endosperm starts indeed at the periphery of the embryosac, appears e.g. from an ovule, collected on September 19. Here the size of the whole endosperm is greater than in the already mentioned ovules (diameter 1,35 mm.), so that only a very narrow layer of nucellus-tissue is visible all round, mostly at the chalaza (greatest diameter of the nucellus 1,4 mm.); but the whole endosperm is hollow and in this cavity remnants of the protoplasm of the embryosac are visible. The endosperm-cells are here of very different sizes and so also the nuclei vary much. Some of them look normal, show karyokinesis, others are enlarged, have assumed all sorts of capricious shapes, the number of nucleoli has greatly increased and a number of fragmentation stages can be observed.

Two ovules, collected on September 10, show a still further developed endosperm. The nucellus tissue has been more displaced, the shape of the endosperm-cells is pretty regular, their cell-wall is somewhat thickened, the nuclei are almost normal; in any case there is much less indication of fragmentation than with the just mentioned ovule.

In an ovule, collected on September 19, the endosperm is so strongly developed that of the nucellus tissue hardly anything remains visible. This also applies to the cases which will be described presently. The endosperm-cells have strongly thickened but still fairly gelatinous walls; the contents of the cells consist of a number

of small grains which stained very strongly and which somehow make the impression of nucleoli; of a nucleus nothing is found any longer, unless we apply the name to some thick, coloured masses.

Three ovules, fixed on December 15, all showed the same picture. A strongly developed endosperm is present with very thick cell-walls, absorbing saffranine more or less, and protoplasts which are entirely foamy and in which nothing of a finer structure is found. This endosperm must evidently be reckoned among the horny ones; it was extremely difficult to cut. Sections of the ovules could only be made after treatment with hydrofluoric acid. It is not impossible, of course, that the foamy appearance of the protoplasts must be ascribed to this treatment, although we do not think this probable on account of other experience with this method. In the endosperm some fissures are visible, the last remnants of the cavity of the embryosac.

Finally an ovule with an endosperm was found among the material collected on January 19. Here also cutting was only possible after treatment with hydrofluoric acid. The endosperm is entirely disorganised, borders of cells can scarcely be recognised. No more than in the preceding cases we think this must be ascribed to the manner of treatment.

We have now described all cases of formation of an endosperm, observed by us. It will have been noticed that the order is not chronological, the arrangement was such that we gradually proceeded from the least developed to the complete endosperm. From this it follows already that the formation of an endosperm takes place very irregularly with these ovules, sets in now sooner, then later, and that the endosperm may pass into disorganisation at various stages of development.

Summarising, it appears that with *Dasyliirion acrotrichum* an endosperm is formed without fertilisation. This endosperm finally disorganises; it may do so already at a pretty early stage of development, but it may also first attain its complete development. But an embryo could never be found together with such an endosperm. From this it does not follow, however, that it could never be formed together with an endosperm, especially since in three ovules — in which, to be sure, no endosperm was formed — in the top of the embryosac a cell-body was found which we take to be an embryo, which however very soon passes into a state of disorganisation.

One may now ask to what cause this disorganisation must be ascribed. It might be suspected that the circumstances of this *Dasyliirion* were abnormal. Although we grant that these were different from

the conditions in the mother country of the plant, yet we must remark that the plant was in the open air for a long time before and after it had bloomed during the very hot summer of 1904 and that there was no question of this specimen being sickly. We venture another supposition: to us it seems that this plant makes, so to say, an attempt to apogamous development, but that these endeavours do not succeed. For this would plead that the endosperm develops here independently of an eventual formation of an embryo and that the embryo is sometimes planned, but never grows to any considerable size. If this be the case, in the mother country of the plant similar phenomena should be observed, but at the same time normal fertilisation and seed-formation. We ought to know the development of the embryosac, in order to know why the apogamy is unsuccessful here, even though the plant makes an attempt in this direction. If in the embryosac mother-cell a reduction division has taken place, this would be very easy to understand and it would also explain the greater facility with which the endosperm is formed. For, after fusion of the two polar nuclei the normal number of chromosomes of the $2x$ -generation (not, of course, of the endosperm) would be re-established again; we have tried to determine this number and it seemed to us to be 20 to 24. But as long as we do not know how the endosperm is formed this determination is of little value; for we owe to TREUB¹⁾ the knowledge of a case of endosperm formation, with *Balanophora elongata*, where the endosperm nuclei are formed by division of one of the two polar nuclei. It is, to be sure, the only case on record where an embryosac fills with endosperm, without a normal embryo being formed. In this respect the ovules of *Dasyllirion*, described by us, could be compared with *Balanophora*. On the other hand there is this great difference, that with *Balanophora* an embryo is later formed from part of the endosperm and of this there is no question with *Dasyllirion*.

We put the word apogamy at the head of this communication because it leaves unsettled whether here phenomena of parthenogenesis were indeed observed. It is an open question to what extent the development of an endosperm without previous fusion of the polar nuclei with one of the generative nuclei of the pollen tube can be brought under one of these conceptions. Those who will not use the word fertilisation in the case of endosperm formation, like STRASBURGER, will object to it; those who embrace the opposite view,

¹⁾ M. TREUB. L'organe femelle et l'Apogamie du *Balanophora elongata* Bl. Ann. du Jardin botan. de Buitenzorg XV. 1898 p. 1. See also J. P. LOTSCH, *Balanophora globosa* Jungh. Ann. du Jardin botan. de Buitenzorg 2me Série I. 1899, p. 174.

like GUIGNARD and BONNIER, will think the use of these terms admissible. Although we incline towards this latter opinion, we shall not dwell on this point here.

But we think it desirable to point out that a closer study of unfertilised ovules, especially of dioecious plants will perhaps yield surprising results. Since we know through LOEB that chemical stimuli may cause the development of an egg, the possibility must be granted that this may also be the case with higher plants. When a normal fertilisation does not take place, such chemical stimuli would at any rate render a beginning of development possible. Looked at from this point of view the case of *Dasyliirion* is perhaps important, but, as we stated already at the beginning of this communication, only an investigation in the natural place of occurrence of the plant can give an answer to this and allied questions.

Astronomy. — "*On the parallax of the nebulae*". By Prof. J. C. KAPTEYN.

Up to the present time we know hardly anything about the distance of the nebulae. On the whole they do not allow of the most accurate measurement, and as a consequence direct determination of parallax is generally to be considered as hopeless. A few endeavours made for particularly regular nebulae have not led to any positive result.

The proper motions (p. m.) seem more promising, at least for the purpose of getting general notions about the distances of these objects.

Spectroscopic measurements of radial motion show that the real velocities of the nebulae are quite of the order of those of the stars. Therefore, as soon as we find the astronomical proper motion of any nebula, we conclude, with some degree of probability, that its distance is of the order of that of the stars with equal p. m.

Meanwhile it may be considered to be a fact, most clearly brought out just by the observations presently to be discussed, that as yet p. m. of a nebula has not been proved with certainty in a single case. It does not follow that these p. m. are necessarily very small. The time during which the position of these bodies has been determined with precision, is still short, the errors of the observations are large. The effect of these errors on the annual p. m. may easily amount to 0".2 or 0".3.

We might endeavour to lessen the influence of the errors of observation by determining *not* the individual motions but the *mean* p. m. of a considerable number of nebulae.

If this succeeded we might then compare this mean p. m. with the mean p. m. of different classes of stars, the mean distance of which is known with some approximation or, better perhaps, with the mean radial velocity of the nebulae determined by the spectro-scope. The comparison would lead at once to ideas about the real distances.

Unfortunately the mean of a great number of *observed* p. m. will not be materially more correct than the individual values, if the total proper motion is small. The cause of this lies in the fact that in such a case the effect of a determined error of observation is not at all cancelled by an equal but opposite error of observation. Suppose for instance two nebulae both having in reality a p. m. of $0^{\circ}01$. For the first let the error of observation be $0^{\circ}10$ in the direction of the p. m. For the second assume an equal error in a direction opposed to the p. m. The *observed* p. m. of the first nebula will be $0^{\circ}11$, that of the second $0^{\circ}09$. Taking the mean of the two we are not brought nearer to the real value.

For this reason we shall not be led to any valuable result in this way, even if our material consists of very numerous objects, as long as the errors of observation exceed the real p. m.

The difficulty here considered would vanish if, instead of the total p. m., we could avail ourselves of some *component* of the p. m., which in different direction would have different sign. In this case, if systematic errors can be avoided or determined, the accuracy would increase as the square root of the number of objects included.

Such a *component* of the p. m. is that in the direction towards the Antapex. From this component we may derive the mean parallax p. m. which is a measure of the mean parallax.

I will not here stop to consider the hypothesis involved. It must be sufficient to state that it assumes that the sum of the projections on some determined direction of the *peculiar* p. m. vanishes in the case of very numerous nebulae or, which comes much to the same that the peculiar p. m. may be treated as errors of observations.

Let

h be the linear annual motion of the solar system ;

ρ the distance of a nebula from that system ;

λ the angular distance of this nebula from the Apex of the solar motion ;

v , τ the components of the observed p. m. in the direction towards the Antapex and at right angles to that direction ;

p the component of the *peculiar* p. m. in the direction towards the Antapex.

The parallactic p. m. shall then be :

$$\frac{h}{\varrho} \sin \lambda = v - p.$$

If this equation is written out for each individual nebula and if, after that, we take the mean of all the equations, the quantities p will disappear and we obtain the mean value of $\frac{h}{\varrho}$, which is the secular parallax.

Or rather :

As we may treat the quantities p as if they were errors of observation, which mix up with the real errors of the observed quantities v , we may write out for each nebula an equation of the form

$$\frac{h}{\varrho} \sin \lambda = v (1)$$

If then we assume that the distance ϱ is the same for all the nebulae, we may solve the whole of the equations (1) by the method of least squares.

I have long wished to apply this method in order to get some more certainty about the position of the nebulae in space, but I have been restrained by the extent of the work connected with such an enterprise.

The difficulty has disappeared since the publication, a few years ago, of a paper by Dr. MÖNNICHMEYER assistant at the Observatory of Bonn (*Veröff. der Kön. Sternw. zu Bonn.* N°. 1). In this paper all the materials available at the time of its appearance have been brought together in a way which, for my purpose, leaves little to be desired.

This paper contains the observations of Dr. MÖNNICHMEYER himself. They bear on no less than 208 objects, mostly chosen among such nebulae as can be measured with considerable or at least moderate precision. Dr. MÖNNICHMEYER has collected besides, all previous observations of these objects. I have confined myself to the observations of those nebulae for which all the observers have used the same star or stars of comparison. I have further rejected the observations of those objects for which MÖNNICHMEYER did not succeed in determining the personal errors. The observations which thus have served for the investigation are those of MÖNNICHMEYER's paper pages 59—70, from which have been excluded, in the first place, those objects which in the list of pages 15—17, second column, have been denoted by the letter M; further the planetary nebulae, the clusters and the ring-nebula h 2023.

There remain 168 nebulae.

A good judgment about the accuracy of the observations may be obtained by the probable error derived by MÖNNICHMEYER for his own observations on page 9. For the other observers I have availed myself of the data contained on pages 18—25.

The accuracy was found little different for the several observers with the exception of RÜMKER.

I therefore simply assumed the weights to be proportional to the number of observations. For RÜMKER only the weight was reduced in the proportion of three to one. For SCHMIDT the number of observations is not given. For reasons given by MÖNNICHMEYER they are "immerhin etwas fraglich" (l. c. page 14). The results of SCHMIDT got the weight of only a single observation for that reason.

An overwhelming majority of the observations has been made between 1861—1869 and 1883—1893. It was possible therefore in nearly every case to contract all the observations in *two* normal differences from which the proper motion and its weight could be derived at once without any serious loss of accuracy.

From these p.m. I then derived the components τ and v , assuming for the position of the Apex, the coordinates

$$A_{75} = 273^\circ, D_{75} = +29^\circ 5'.$$

The whole of the materials was divided into the three classes of MÖNNICHMEYER. They are described by him on page 9 of his paper in the following way:

Class I. Nebulae with starlike nucleus not fainter than 11th magnitude;

Class II. Nebulae with moderately condensed nucleus not fainter than 11th magnitude;

Class III. Difficult objects, in the first place irregular nebulae without any sharply marked point; furthermore all very faint objects and the very oblong nebulae.

Most of the objects have been classified by MÖNNICHMEYER himself on page 9 of his paper. The nebulae wanting in this list have been classified by myself, in accordance with the descriptions on p.p. 27—54, as follows: h 693, 1088, 1225 in Class I; h 421, 1017, 1212, 1221, 1251, 3683 in Class II; h 316, 1461 in Class III.

The p.m. as derived are relative p.m.; they are the motions relative to the comparison stars. MÖNNICHMEYER has investigated the p.m. of the comparison stars themselves; he has found a sensible p.m. for only 7 of the objects used for my investigation. The following table contains his results for these 7 stars.

Star of Comp.	mag.	used for nebula	μ_{α}	μ_{δ}	p. m. in arc gr. circle	v	Sin λ
15	6.0	h 132	^s + 0.0140	["] - 0.089	["] 0.227	["] + 0.225	0.94
90	8.8	h 805	+ .0237	- .170	.352	- .156	1.00
129	6.1	h 1171	- .0170	- .127	.257	+ .255	0.97
164	7.1	h 1329	- .013	.00	.192	+ .167	0.99
168	9.5	M 90	+ .014	.00	.204	- .180	0.98
208	4.7	II 542	- .0050	+ .010	.075	+ .055	0.80
242	6.6	h 2050	- .0134	- .152	.199	- .197	0.45

These p. m. were applied by MÖNNICHMEYER before he derived his definitive differences in α and δ (Neb.-Star). In no other case a correction for the p. m. of the comparison stars was applied.

The majority of the observers used the ringmicrometer.

The principal error to be feared for observation with this micrometer is the personal error in right ascension. MÖNNICHMEYER has devoted the utmost care to their determination. Notwithstanding this it may be considered a fortunate circumstance that this error has no influence on the result for the mean parallactic motion, at least in the ideal case that the nebulae are distributed uniformly over the right ascensions from 0 to 24 hours.

For it seems highly probable that the distance of the nebulae is not systematically different in the different hours of right ascension. This being so the personal error will vitiate the parallactic p. m. of the nebulae at the same distance in right ascension on both sides of the apex, to the same extent but in opposite directions.

It is true that the distribution in right ascension is far from being uniform; still we may be sure that whatever residual personal errors may still exist in the materials of MÖNNICHMEYER, must appear considerably diminished in the result. Meanwhile I have tried to obtain some idea about the possible amount of these residual errors in the following way.

I computed the average proper motion in right ascension for each hour separately. Taking the simple mean of all these hourly averages we may expect to get a result in which not only the peculiar proper motions, but, as explained just now, also the parallactic motions shall have vanished.

This final result may therefore be assumed to represent the residual influence of the personal errors on the p.m.

For the value $\overline{\mu}_\alpha$ of this mean I find

$$\overline{\mu}_\alpha = -0.0004$$

In deriving this result the hours with many nebulae did not get any greater weight than the hours with only a few objects. Owing to this cause the final weight is found to be only 0.4 of what it would have been had the distribution been uniform.

We shall get a result of appreciably greater weight if in the first place we combine by twos the hours lying symmetrically in respect to the apex. In these mean values the parallactic motion is already eliminated; we may therefore further combine the twelve partial results having regard to their individual weights.

In this way I find

$$\overline{\mu}_\alpha = +0.0006.$$

It thus appears that MÖNNICHMEYER has succeeded remarkably well in getting rid of the influence of the personal errors.

As mentioned just now these errors appear still further diminished in the result for the parallactic motion.

There thus seems to be ample reason for neglecting any further consideration of them. In order to enable the reader to get at once a pretty good insight in the accuracy really obtained, I have divided the whole of the material not only into the three classes [of MÖNNICHMEYER, but I have subdivided each of them into a certain number of sections, each of about the same weight.

I thus got the following summary. (See p. 697).

The values of τ have been included in the table merely in order to show that in them too no traces of any personal error are visible.

In order to get the yearly parallaxes π , I have divided the secular parallaxes $\frac{h}{\rho}$ by 4.20; this number being, according to CAMPBELL's determination, the number of solar distances covered by the solar system in a year in its motion through space.

The probable errors were derived in the hypothesis that the component v is wholly due to errors of observation.

If we compute the probable error of one of our 13 results from their internal agreement we get 0."023. This number differs very little from the values directly found. Here again we have an indication that systematic errors must be small.

The last row of numbers contains the simple averages of the 13 individual results.

Class	α	numb of neb.	τ	$\frac{h}{\rho}$	$p.e.$	π	$p.e.$
	$h^m \quad h^m$		"	"	"	"	"
I	0.0 — 5.33	13	+ 0.014	— 0.039	± 0.023	— 0.009	$\pm 0.005^s$
	5.33—10.57	12	— .043 ^s	+ .051	.022	+ .012	5
	10.57—12.22	10	— .045	+ .034	.023	+ .008	5 ^s
	12.22—12.45	9	— .004	— .027	.022	— .006 ^s	5
	12.45— 0. 0	10	— .008	+ .013	.023	+ .003	5 ^s
II	0.0 — 9.50	12	+ .021	+ 0.014	± 0.019	+ .003	4 ^s
	9.50—11.10	10	— .004	— .016	.019	— .004	4 ^s
	11.10—12.16	11	— .008	— .037	.020	— .009	5
	12.16—12.28	12	+ .019	— .040	.020	— .009 ^s	5
	12.28— 0. 0	14	+ .000 ^s	— .040	.020	— .009 ^s	5
III	0.0 —12.14	20	+ .030	+ 0.016	± 0.019	+ .004	4 ^s
	12.14—12.32	16	— .046	+ .038	.019	+ .009	4 ^s
	12.32— 0. 0	19	+ .016	— .036 ^s	.018	— .009	4
Simple mean of 13 results		168	— 0.004	— 0.005	± 0.005	— .0013	± 0.0012

We thus finally get for the mean yearly parallax

$$- 0''.0013 \pm 0''.0012 \text{ (168 nebulae).} \quad (3)$$

This is the parallax relative to stars of comparison the mean magnitude of which is

8.75

Meanwhile, as mentioned before, MÖNNICHMEYER applied p. m. to 7 of his 183 stars of comparison.

If he had refrained from doing so, we should have found the parallax $0''.0004$ smaller. We thus have in conclusion:

Mean parallax of the 168 nebulae relative to stars of comparison of the mean magnitude 8.75.

$$- 0''.0017 \pm 0''.012 \text{ (p. e.).} \quad (4)$$

In N°. 8 of the *Publ. of the Astr. Laboratory at Groningen* the mean parallax of the stars of magnitude 8.75 was found to be

$$0''.0063 \quad (5)$$

To this value we might apply two corrections:

1st. Because, since the publication of the paper mentioned, our knowledge about the sun's velocity has made considerable progress;

2nd. Because in its derivation a slight mistake was discovered.

I shall not apply any correction, however, because the two corrections nearly compensate each other for the magnitude 8.75. There is a fair prospect of the possibility of materially improving the values given in Publication 8 before long. It seems advisable to wait for such improvements before we alter these determinations.

If for this reason we provisionally adopt the value (5) we get:

Mean *absolute* parallax of the 168 nebulae

$$0''0046 \pm 0''0012 \text{ (p. e.)} \quad (6)$$

This result is somewhat less reliable, however, than (5) because of the additional uncertainty in the absolute parallax of the stars of comparison.

The value (6) agrees nearly with the mean parallax of the stars of the tenth magnitude.

I shall not insist on the exact amount brought out for the parallax. I shall only direct the attention to the fact that from observations covering only a period of somewhat over thirty years, we get a probable error of hardly over $0''.001$. If this is the case with visual observations we may look for really excellent results by photography.

The best measurable nebulae must be generally the smaller ones. The number of these which can be photographed is enormous.

With his Bruce-telescope (opening 40 centim., foc. dist. 202 centim.) MAX WOLFF obtained in 150 minutes a single photograph of the region near 31 Comae, containing 1528 measurable nebulae (Publ. Königstuhl I p. 127).

This richness of material will enable us to confine ourselves provisionally to those nebulae which allow of a very accurate measurement.

Personal errors must disappear because we shall certainly succeed in nearly every case in making our pointings on the same point for the several epochs. The peculiar p. m. will be the more thoroughly eliminated the more extensive our material; especially if this material is distributed over the whole of the sky. Errors in the precession have no influence at least on the value of the relative parallax.

I am convinced that by photography we may obtain, even within ten years, results which will far surpass in accuracy those of the present paper. Thus we may hope, in the near future, to reach a fairly satisfactory solution of the vexed question respecting the position of the nebulae in space.

The same treatment to which we have here subjected the nebulae may of course also be applied to other objects. We have already

undertaken that of the Helium-stars and might perhaps afterwards try the same method for the stars of PICKERING's 5th Type.

In concluding it is only just to say that, whatever be the merit of the present investigation, it belongs mainly to Dr. MÖNNICHMEYER. As compared with his careful and elaborate labour, that spent on the derivation of the present result is quite insignificant.

Chemistry. — “*On the course of melting-point curves for compounds which are partially dissociated in the liquid phase, the proportion of the products of dissociation being arbitrary*”, by J. J. VAN LAAR. (Communicated by Prof. H. W. BAKHUIS ROOZEBOOM).

1. It is well known, that a liquid mixture of e. g. two components A and B , which can form a compound $A_n B_m$, reaches its *maximum point of solidification*, when the ratio of the molecular quantities of the two components is as $v_1 : v_2$, in other words when there is *no excess* of one of the products of dissociation of the compound $A_n B_m$.

Expressed differently: when we determine the points of solidification of a series of liquid mixtures of A , B and the compound with increasing excess x of one of the products of dissociation of the compound under consideration, then $\left(\frac{dT}{dx}\right)_0 = 0$ for the curve of solidification or melting-point line thus formed.

Hence the melting-point curve of a compound, with increasing addition x of one of the products of dissociation, will have an *horizontal* direction at $x = 0$, as soon as there is but the *slightest dissociation* of the compound in the liquid phase. If there is *no dissociation at all*, the admixture may be considered as an alien, indifferent substance, and the initial direction of the melting-point curve will show *all at once the normal descending course* at $x = 0$.

As will also appear from the following computation, the initial horizontal course will of course pass the sooner into a descending course, the slighter the dissociation of the compound is.

The peculiarity mentioned of $\left(\frac{dT}{dx}\right)_0$ becoming zero with the slightest trace of dissociation of the compound, was already proved by Prof. LORENTZ in 1892, on the occasion of an investigation of STORTENBEKER on chlorine-iodides ¹⁾. Prof. VAN DER WAALS too has

¹⁾ Z. f. Ph. Ch. 10, bl. 194 et seq.

proved this property, induced by a statement made by LE CHATELIER¹⁾. The proof given does not directly bear, however, on the case that in the liquid phase also the *compound* (VAN DER WAALS' so-called complex molecule of salt and water) is found by the side of the products of dissociation.

2. Here follows another simple and quite general proof of the property in question, in which specially the condition in the liquid phase is taken into consideration, in which by the side of the compound the products of dissociation occur in varying quantities.

Let us suppose there *three* kinds of molecules:

those of the compound $A_n B_x$; number $n_0 = 1 - \alpha$

those of A ; „ $n_1 = v_1 \alpha$

those of B ; „ $n_2 = v_2 \alpha + x$.

So α is the degree of dissociation of the compound, and x the excess of B e.g.

Now from the property, that the molecular potentials of these three substances, viz. μ_0 , μ_1 and μ_2 , are *homogeneous* functions of the 0th degree with respect to the numbers of molecules, follows immediately:

$$n_0 \frac{d\mu_0}{dx} + n_1 \frac{d\mu_1}{dx} + n_2 \frac{d\mu_2}{dx} = 0 \quad (1)$$

Here the differentiations with respect to x are to be taken total, so that e.g.:

$$\frac{d\mu_0}{dx} = \frac{\partial \mu_0}{\partial x} + \frac{\partial \mu_0}{\partial \alpha} \frac{d\alpha}{dx},$$

i.e. at constant temperature.

[The above property is proved (loc. cit.) as follows. We have viz. in consequence of the mentioned peculiarity of the functions μ_0 , μ_1 and μ_2 :

$$\left. \begin{aligned} n_0 \frac{\partial \mu_0}{\partial n_0} + n_1 \frac{\partial \mu_0}{\partial n_1} + n_2 \frac{\partial \mu_0}{\partial n_2} &= 0 \\ n_0 \frac{\partial \mu_1}{\partial n_0} + n_1 \frac{\partial \mu_1}{\partial n_1} + n_2 \frac{\partial \mu_1}{\partial n_2} &= 0 \\ \dots \dots \dots \end{aligned} \right\}$$

So also $\frac{\partial \mu_1}{\partial n_2}$ being equal to $\frac{\partial \mu_2}{\partial n_1}$, etc. (for $\mu_1 = \frac{\partial Z}{\partial n_1}$ and $\mu_2 = \frac{\partial Z}{\partial n_2}$).

¹⁾ Verslagen Kon. Akad. van Wetenschappen (4) V, p. 385 (1897).

²⁾ These and the following properties were already proved by me in 1894. See Z. f. Ph. Ch. 15, p. 459 et seq. ("Ueber die genauen Formeln, etc.").

$$\left. \begin{aligned} n_0 \frac{\partial \mu_0}{\partial n_0} + n_1 \frac{\partial \mu_1}{\partial n_0} + n_2 \frac{\partial \mu_2}{\partial n_0} &= 0 \\ n_0 \frac{\partial \mu_0}{\partial n_1} + n_1 \frac{\partial \mu_1}{\partial n_1} + n_2 \frac{\partial \mu_2}{\partial n_1} &= 0 \end{aligned} \right\}.$$

So if we pass from the variables n_0 , n_1 and n_2 (of which there are only two independently variable) to the variables α and x , we have also:

$$\left. \begin{aligned} n_0 \frac{\partial \mu_0}{\partial \alpha} + n_1 \frac{\partial \mu_1}{\partial \alpha} + n_2 \frac{\partial \mu_2}{\partial \alpha} &= 0 \\ n_0 \frac{\partial \mu_0}{\partial x} + n_1 \frac{\partial \mu_1}{\partial x} + n_2 \frac{\partial \mu_2}{\partial x} &= 0 \end{aligned} \right\}^{1)}$$

The first equation multiplied by $\frac{d\alpha}{dx}$ and added to the second, gives immediately (1).]

Now follows from the equilibrium of dissociation:

$$-\mu_0 + v_1 \mu_1 + v_2 \mu_2 = 0$$

¹⁾ We can easily test the truth of these simple properties by supposing the functions μ'_0 , μ'_1 and μ'_2 constant in:

$$\mu_0 = \mu'_0 + RT \log \frac{1-\alpha}{N}, \quad \mu_1 = \mu'_1 + RT \log \frac{v_1 \alpha}{N},$$

$$\mu_2 = \mu'_2 + RT \log \frac{v_2 \alpha + x}{N}.$$

Then we have immediately (having divided by RT) after differentiation $\frac{\partial}{\partial \alpha}$, taking into consideration that

$$N = 1 + (v_1 + v_2 - 1)\alpha + x = 1 + \theta\alpha + x,$$

for the first member:

$$\begin{aligned} (1-\alpha) \left\{ -\frac{1}{1-\alpha} - \frac{\theta}{N} \right\} + v_1 \alpha \left\{ \frac{1}{\alpha} - \frac{\theta}{N} \right\} + (v_2 \alpha + x) \left\{ \frac{v_2}{v_2 \alpha + x} - \frac{\theta}{N} \right\} = \\ = (-1 + v_1 + v_2) - \frac{\theta}{N} (1 - \alpha + v_1 \alpha + v_2 \alpha + x) = \theta - \frac{\theta}{N} \times N = 0. \end{aligned}$$

After differentiation $\frac{\partial}{\partial x}$ we find for the first member:

$$\begin{aligned} (1-\alpha) \left\{ -\frac{1}{N} \right\} + v_1 \alpha \left\{ -\frac{1}{N} \right\} + (v_2 \alpha + x) \left\{ \frac{1}{v_2 \alpha + x} - \frac{1}{N} \right\} = \\ = 1 - \frac{1}{N} (1 - \alpha + v_1 \alpha + v_2 \alpha + x) = 1 - \frac{1}{N} \times N = 0. \end{aligned}$$

And according to what has been proved, this will continue to be true, also when μ'_0 , μ'_1 and μ'_2 are still functions of α and x .

immediately, after total differentiation with respect to x (T constant):

$$-\frac{d\mu_0}{dx} + v_1 \frac{d\mu_1}{dx} + v_2 \frac{d\mu_2}{dx} = 0 \quad \dots \quad (2)$$

And from (1) and (2) follows, that when $n_1:n_2=v_1:v_2$ (i.e. $x=0$), we have necessarily

$$\frac{d\mu_0}{dx} = 0 \quad \dots \quad (3)$$

So the *becoming zero* of $\frac{d\mu_0}{dx}$ is the *primary moment*, on account of which also $\left(\frac{dT}{dx}\right)_0$ will have to be 0 in the presence of a solid phase: with change of x (with which also α changes) the *mol. potential of the unsplit compound does, namely, not change when $x=0$* . [This property will evidently also continue to hold for an arbitrary number of splitting products].

That now also $\left(\frac{dT}{dx}\right)_0 = 0$, follows from the *condition of equilibrium*:

$$-\mu + \mu_0 = 0,$$

when μ is the mol. potential of the solid phase. Total differentiation with respect to T yields viz.:

$$\frac{d}{dT}(-\mu + \mu_0) + \frac{d}{dx}(-\mu + \mu_0) \frac{dx}{dT} = 0,$$

in which $\frac{d}{dT}$ is again $\left(\frac{\partial}{\partial T} + \frac{\partial}{\partial \alpha} \frac{d\alpha}{dT}\right)_x$, and $\frac{d}{dx} = \left(\frac{\partial}{\partial x} + \frac{\partial}{\partial \alpha} \frac{d\alpha}{dx}\right)_T$.

But $\frac{d}{dT}(-\mu + \mu_0) = -\frac{Q}{T}$, when Q is the *total heat of melting*, hence also:

$$-\frac{Q}{T} + \frac{d\mu_0}{dx} \frac{dx}{dT} = 0,$$

because μ (in the solid phase) is independent of x . Hence:

$$\frac{dT}{dx} = \frac{T \frac{d\mu_0}{dx}}{Q} \quad \dots \quad (4)$$

So if $\frac{d\mu_0}{dx} = 0$, also $\frac{dT}{dx} = 0$, and in this way the proposition is proved. When in the liquid phase there is *no excess* of one of the products of dissociation, but instead an indifferent substance, then there are *four* kinds of molecules, with molecular quantities resp.:

$$1 - \alpha, \quad v_1 \alpha, \quad v_2 \alpha, \quad x.$$

Instead of (1) we get now :

$$n_0 \frac{d\mu_0}{dx} + n_1 \frac{d\mu_1}{dx} + n_2 \frac{d\mu_2}{dx} + n_3 \frac{d\mu_3}{dx} = 0^1). \quad (1^a)$$

And as $n_3 \frac{d\mu_3}{dx} = x \frac{d\mu_3}{dx}$ remains *finite* at $x=0$, viz. RT , from (1^a)

and (2) will now *not* follow $\frac{d\mu_0}{dx} = 0$, when $x=0$. ($n_1 : n_2 = v_1 : v_2$,

is always satisfied in this case). And consequently $\frac{dT}{dx}$ will *not* be 0.

[That $x \frac{d\mu_3}{dx}$ continues to have a finite value at $x=0$, follows from this,

that $\mu_3 = \mu'_3 + RT \log \frac{x}{N}$ yields $\frac{d\mu_3}{dx} = \frac{d\mu'_3}{dx} + \frac{RT}{x} - \frac{RT}{N} \frac{dN}{dx}$, hence

$x \frac{d\mu_3}{dx} = RT + x \left\{ \frac{d\mu'_3}{dx} - \frac{RT}{N} \frac{dN}{dx} \right\}$, in which the expression between $\left\{ \right\}$

always remains finite. At $x=0$ we have therefore $x \frac{d\mu_3}{dx} = RT$].

3. We now proceed to derive an expression for the course of the melting-point curve in the case of increasing excess of one of the products of dissociation in the liquid phase.

Let us for this purpose suppose, that in this phase there are present (in Gr. mol.) $1-x$ AB and x B , while the $1-x$ AB is dissociated to an amount α . We have then :

$$\begin{array}{ccc} AB & A & B \\ (1-\alpha)(1-x) & \alpha(1-x) & \alpha(1-x) + x, \end{array}$$

together $1 + \alpha(1-x)$ molecules.

We suppose then, that the compound consists of 1 mol. A and 1 mol. B , which simplifies the calculations.

The equilibrium between the solid phase and the non-dissociated molecules in the liquid phase yields:

$$\mu = \mu_0,$$

or (the terms with $T \log T$ on either side cancel each other)

$$\varepsilon - cT = \varepsilon_0 - c_0T + RT \log \frac{(1-\alpha)(1-x)}{1 + \alpha(1-x)},$$

¹⁾ This too is easy to test, when μ'_0, μ'_1 , etc. are considered as constant, so that e.g. in

$$\mu_0 = \mu'_0 + RT \log \frac{1-\alpha}{N}, \quad \frac{\partial \mu_0}{\partial \alpha} \text{ becomes } = RT \left\{ -\frac{1}{1-\alpha} - \frac{\theta}{N} \right\} \text{ etc.}$$

or with $\varepsilon_0 - \varepsilon = \left(e_0 - \frac{a_0}{b_0}\right) - \left(e_0 - \frac{a}{b}\right) = \left(e_0 + kT - \frac{a_0}{b_0}\right) - \left(e_0 + kT - \frac{a}{b}\right) = q$ (so that q is the pure latent heat of melting of the compound, without the heat of dissociation, which is still to be added), and with $c_0 - c = \gamma$:

$$q = \gamma T - RT \log \frac{(1-\alpha)(1-x)}{1+\alpha(1-x)}.$$

For the determination of γ may serve, that at $x=0$ and $T=T_0$, α becomes α_0 , hence:

$$q = \gamma T_0 - RT_0 \log \frac{1-\alpha_0}{1+\alpha_0}.$$

Hence we finally get:

$$q(T_0 - T) = -RTT_0 \log \frac{1+\alpha_0}{1-\alpha_0} \frac{(1-\alpha)(1-x)}{1+\alpha(1-x)},$$

or

$$-\log \frac{1+\alpha_0}{1-\alpha_0} \frac{(1-\alpha)(1-x)}{1+\alpha(1-x)} = \frac{q}{R} \left(\frac{1}{T} - \frac{1}{T_0} \right). \quad (5)$$

In this derivation it has also been supposed, that the liquid mixture is a so-called *ideal* mixture, i. e. that terms, referring to the influence of the components inter se, have been left out. It is known that these terms are of the *second* degree with respect to x . Equation (5) represents therefore the course of the "ideal" melting-point curve in our case.

Further the degree of dissociation α occurring there is given by the equation (here too the above mentioned terms are left out, so that the simple law of mass-action is supposed to hold):

$$\frac{\alpha(1-x)}{N} \times \frac{\alpha(1-x)+x}{N} : \frac{(1-\alpha)(1-x)}{N} = K,$$

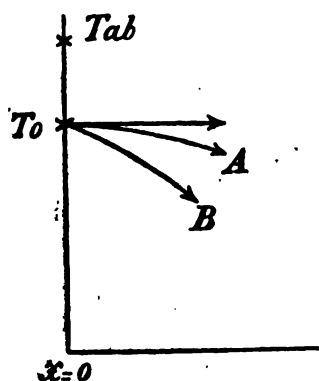
or

$$\frac{\alpha(\alpha(1-x)+x)}{(1-\alpha)(1+\alpha(1-x))} = K. \quad (6)$$

In this K is now no longer a function of x according to the above supposition, but it is one of T .

Even if we would solve α from this quadratic equation, and substitute it in (5), we should have gained but little, because K contains T in a rather intricate way. Therefore the only thing we can do, is to try and find an *approximate* expression, which only holds for *small* values of x .

After that a general expression for $\frac{dT}{dx}$ will be given.



In order to find the approximate expression in question for the course of the curve T_0A , we suppose for the present, that α does vary with x , but not with T . In the result we have then simply to replace q by the *total* heat of melting at $x=0$ $Q_0 = q + \alpha_0 \lambda$ (λ is the *heat of dissociation*), in order to introduce the variability of α with T . (see appendix).

From (6) follows now immediately the quadratic equation

$$\alpha^2(1-x) + \alpha x - \frac{K}{1+K} = 0.$$

By putting $x=0$, we see that $\frac{K}{1+K}$ is then $= \alpha_0^2$. According to the above provisional assumption it is now supposed, that also for values of T , lower than T_0 , the value of α_0 holding for $x=0$ and $T=T_0$, remains unchanged. Therefore in the equation

$$\alpha^2(1-x) + \alpha x - \alpha_0^2 = 0$$

α_0 is no longer a function of T . So we find for α :

$$\alpha = \frac{-\frac{1}{2}x + \sqrt{\frac{1}{4}x^2 + \alpha_0^2(1-x)}}{1-x},$$

and hence

$$1-\alpha = \frac{1 - \frac{1}{2}x - \sqrt{\frac{1}{4}x^2 + \alpha_0^2(1-x)}}{1-x}.$$

In consequence of this we get:

$$\left. \begin{aligned} (1-\alpha)(1-x) &= 1 - \frac{1}{2}x - \sqrt{\frac{1}{4}x^2 + \alpha_0^2(1-x)} \\ 1 + \alpha(1-x) &= 1 - \frac{1}{2}x + \sqrt{\frac{1}{4}x^2 + \alpha_0^2(1-x)} \end{aligned} \right\},$$

so that we find for the quotient occurring under the sign log in (5):

$$\frac{1 - \frac{1}{2}x - \sqrt{\frac{1}{4}x^2 + \alpha_0^2(1-x)}}{1 - \frac{1}{2}x + \sqrt{\frac{1}{4}x^2 + \alpha_0^2(1-x)}},$$

or also after multiplication of numerator and denominator by $1 - \frac{1}{2}x - \sqrt{\frac{1}{4}x^2 + \alpha_0^2(1-x)}$:

$$\frac{(1 + \alpha_0^2)(1-x) + \frac{1}{2}x^2 - 2(1 - \frac{1}{2}x)\sqrt{\frac{1}{4}x^2 + \alpha_0^2(1-x)}}{(1 - \alpha_0^2)(1-x)}.$$

Let us now approximate $\sqrt{\alpha_0^2(1-x) + \frac{1}{4}x^2} = \alpha_0 \sqrt{1-x + \frac{1/4 x^2}{\alpha_0^2}}$
for small values of x .

We shall find :

$$\sqrt{1-x + \frac{1/4 x^2}{\alpha_0^2}} = 1 - \frac{1}{2}x + \frac{1}{8} \frac{1-\alpha_0^2}{\alpha_0^2} x^2 + \\ + \frac{1}{16} \frac{1-\alpha_0^2}{\alpha_0^2} x^3 - \frac{1}{128} \frac{(1-\alpha_0^2)(1-5\alpha_0^2)}{\alpha_0^4} x^4 \dots$$

$\alpha_0 \sqrt{\quad}$, multiplied by $2-x$, yields then:

$$\alpha_0 \left[2(1-x) + \frac{1}{4} \frac{1+\alpha_0^2}{\alpha_0^2} x^2 - \frac{1}{64} \left(\frac{1-\alpha_0^2}{\alpha_0^2} \right)^2 x^4 \dots \right].$$

This, subtracted from $(1+\alpha_0^2)(1-x) + \frac{1}{4}x^2$, gives:

$$(1-\alpha_0^2)(1-x) - \frac{1}{4} \frac{(1-\alpha_0^2)^2}{\alpha_0^2} x^2 + \frac{1}{64} \frac{(1-\alpha_0^2)^2}{\alpha_0^2} x^4 \dots$$

If now finally this formula is divided by $(1-\alpha_0^2)(1-x)$, we get:

$$\frac{1-\alpha_0^2}{1+\alpha_0^2} \left\{ 1 - \frac{\frac{1}{4} \frac{x^2}{\alpha_0^2} - \frac{1}{64} \frac{(1+\alpha_0^2)^2}{\alpha_0^2} x^4 \dots}{1-x} \right\}.$$

Equation (5) changes now into:

$$- \log \left\{ 1 - \frac{1}{4} \frac{x^2}{\alpha_0^2} \frac{1 - \frac{1}{64} \frac{(1+\alpha_0^2)^2}{\alpha_0^2} x^4 \dots}{1-x} \right\} = \frac{q}{R} \left(\frac{1}{T} - \frac{1}{T_0} \right).$$

Notice, that the term with x does not occur, in consequence of which $\left(\frac{dT}{dx} \right)_0$ satisfies the condition of becoming 0.

If higher powers than x^2 are neglected, the above becomes:

$$\frac{x^2(1+x)}{4\alpha_0^2} = \frac{q}{R} \left(\frac{1}{T} - \frac{1}{T_0} \right),$$

or also, if we now replace q by Q_0 (see above) and TT_0 by T_0^2 , which does not bring about a change in the coefficient of x^2 , as $T = T_0(1-\theta x^2)$:

$$T_0 - T = \frac{RT_0^2 x^2 (1+x)}{Q_0 4\alpha_0^2}, \quad \dots \dots \dots (5a)$$

which approximate expression holds for not too small values of α (e. g. $\alpha = \frac{1}{2}$) at least up to values of $x = 0.1$. We see, that $T_0 - T$ is not proportional to x , for small values of x , but proportional to x^2 . Hence instead of the usual straight downward course

of the melting-point curve at the beginning, it presents now an almost horizontal course.

Observation.

Equation (5) enables us also to compute the melting-point temperature T_{ab} of the unsplit compound (i. e. unsplit in the liquid phase). (cf. fig. 1).

Then we have namely $\alpha = 0$, $x = 0$, and we get, supposing $\alpha_{ab} = \alpha_0$:

$$-\log \frac{1 + \alpha_0}{1 - \alpha_0} = \frac{q}{R} \left(\frac{1}{T_{ab}} - \frac{1}{T_0} \right),$$

from which follows:

$$\frac{1}{T_{ab}} = \frac{1}{T_0} - \frac{R}{q} \log \frac{1 + \alpha_0}{1 - \alpha_0} \quad \dots \quad (7)$$

4. We shall now derive the general expression for $\frac{dT}{dx}$ all over the line T_0A , in which it is only supposed that we have to do with ideal mixtures in the liquid phase, so that the terms, referring to the influence inter se of the different components, are again left out. But besides on x , α will now also depend on T .

In two different ways we can arrive at the correct expression for $\frac{dT}{dx}$.

First of all by total differentiation of the equation (5) with respect to T . We get then, calling the fraction $\frac{(1 - \alpha)(1 - x)}{1 + \alpha(1 - x)} = c_0$:

$$\left(\frac{d \log c_0}{dT} \right)_x + \left(\frac{d \log c_0}{dx} \right)_T \frac{dx}{dT} = \frac{q}{RT^2},$$

hence

$$\frac{dT}{dx} = \frac{\frac{d \log c_0}{dx}}{\frac{q}{RT^2} - \frac{d \log c_0}{dT}}.$$

$$\begin{aligned} \text{Now } \frac{d \log c_0}{dx} &= \frac{\partial \log c_0}{\partial x} + \frac{\partial \log c_0}{\partial \alpha} \frac{d\alpha}{dx} = \\ &= \left(-\frac{1}{1-x} + \frac{\alpha}{1+\alpha(1-x)} \right) + \left(-\frac{1}{1-\alpha} - \frac{1-x}{1+\alpha(1-x)} \right) \frac{d\alpha}{dx} = \\ &= -\frac{1}{(1-x)(1+\alpha(1-x))} - \frac{2-x}{(1-\alpha)(1+\alpha(1-x))} \frac{d\alpha}{dx}. \end{aligned}$$

Hence we must calculate $\frac{da}{dx}$. From (6) follows:

$$\frac{1}{\alpha} \frac{da}{dx} + \frac{1}{x + \alpha(1-x)} \left\{ 1 - \alpha + (1-x) \frac{da}{dx} \right\} + \frac{1}{1-\alpha} \frac{da}{dx} - \frac{1}{1 + \alpha(1-x)} \left\{ -\alpha + (1-x) \frac{da}{dx} \right\} = 0.$$

After reduction we find from this:

$$\frac{da}{dx} = - \frac{\alpha(1-\alpha)}{x + 2\alpha(1-x)} \quad \dots \quad (a)$$

Substitution yields now:

$$\begin{aligned} \frac{d \log c_0}{dx} &= - \frac{1}{(1-x)(1+\alpha(1-x))} + \frac{\alpha(2-x)}{(1+\alpha(1-x))(x+2\alpha(1-x))} = \\ &= - \frac{x}{(1-x)(x+2\alpha(1-x))}. \end{aligned}$$

For $\frac{d \log c_0}{dT}$ we find in the same way:

$$\frac{d \log c_0}{dT} = \frac{\partial \log c_0}{\partial T} + \frac{\partial \log c_0}{\partial \alpha} \frac{da}{dT} = \frac{\partial \log c_0}{\partial \alpha} \frac{da}{dT},$$

because c_0 is not directly dependent on T . This gives further (see above):

$$\frac{d \log c_0}{dT} = - \frac{2-x}{(1-\alpha)(1+\alpha(1-x))} \frac{da}{dT}.$$

So we calculate $\frac{da}{dT}$. From (6) follows:

$$\frac{1}{\alpha} \frac{da}{dT} + \frac{1-x}{x + \alpha(1-x)} \frac{da}{dT} + \frac{1}{1-\alpha} \frac{da}{dT} - \frac{1-x}{1 + \alpha(1-x)} \frac{da}{dT} = \frac{\lambda}{RT^2},$$

as $\frac{\partial \log K}{\partial T} = \frac{\lambda}{RT^2}$, when λ represents the heat of dissociation.

By solution and reduction we find:

$$\frac{da}{dT} = \frac{\lambda}{RT^2} \frac{\alpha(1-\alpha)(1+\alpha(1-x))(x+\alpha(1-x))}{x+2\alpha(1-x)} \quad \dots \quad (b)$$

In consequence of this we get:

$$\frac{d \log c_0}{dT} = - \frac{\lambda}{RT^2} \frac{\alpha(2-x)(x+\alpha(1-x))}{x+2\alpha(1-x)}.$$

If we now substitute the values found for $\frac{d \log c_0}{dx}$ and $\frac{d \log c_0}{dT}$ in

the last equation for $\frac{dT}{dx}$, we get finally:

$$\frac{dT}{dx} = - \frac{RT^2 \frac{1}{1-x} \frac{x}{x+2\alpha(1-x)}}{q + \alpha \frac{(2-x)(x+\alpha(1-x))}{x+2\alpha(1-x)} \lambda}$$

i.e.

$$\frac{dT}{dx} = - \frac{RT^2}{Q} \frac{1}{1-x} \frac{x}{x+2\alpha(1-x)} \quad \dots \quad (8)$$

when for $q +$ etc. is written Q , i. e. the *total* heat of melting.

This formula, combined with (6), indicates therefore the direction of the melting-point curve throughout its course.

In the second place we could have derived the same expression from the general equation (4). As namely $\mu_o = \mu_o' + RT \log c_o$, we have $\frac{d\mu_o}{dx} = \frac{RT \frac{d \log c_o}{dx}}$, assuming μ_o' to be independent of x , and hence:

$$\frac{dT}{dx} = \frac{RT^2 \frac{d \log c_o}{dx}}{Q}$$

Substitution of the above found value of $\frac{d \log c_o}{dx}$ yields immediately (8). But now we have still to prove, that really the total heat Q is represented by

$$Q = q + \alpha \frac{(2-x)(x+\alpha(1-x))}{x+2\alpha(1-x)} \lambda \quad \dots \quad (9)$$

This takes place in the following way. If a quantity dn of solid substance passes into the liquid phase, the total quantity of heat absorbed is evidently:

$$q \, dn + \alpha \lambda \, dn + (1-x) \lambda \frac{d\alpha}{dn} \, dn.$$

For q is the pure latent heat of melting, if only non-dissociated molecules are formed. But of the dn mols. an amount $\alpha \, dn$ is dissociated; the heat required is $\alpha \, dn \cdot \lambda$. Finally the *existing* condition of dissociation α of the $1-x$ mols. will be changed by the addition of dn new mols., namely to an amount $(1-x) \frac{d\alpha}{dn} \, dn$. For $(1-x) \alpha$ dissociated mols. become $(1-x)(\alpha + d\alpha)$.

Now $\frac{da}{dn} = \frac{da}{dx} \frac{dx}{dn}$. And from $1-x=n$, $x=m$ follows $x = \frac{m}{m+n}$,
 hence $\frac{dx}{dn} = -\frac{m}{(m+n)^2} = -x$. So $\frac{da}{dx} = -x \frac{da}{dx}$.

Dividing by dn , we find therefore for the total quantity of heat, absorbed per Gr. mol.:

$$Q = q + a\lambda - x(1-x) \frac{da}{dx} \lambda.$$

Substitution of $\frac{da}{dx}$ from (a) yields then after a slight transformation (9).

Let us now put $x=0$, then we find from (8) on account of the factor x :

$$\left(\frac{dT}{dx}\right)_0 = 0. \quad \dots \quad (8^a)$$

If α is *very small*, this horizontal course does not continue long. For with small x we may write:

$$\frac{dT}{dx} = -\frac{RT^2}{Q} \frac{x}{x+2\alpha}.$$

As soon therefore as x becomes so large that 2α is small with respect to x , the fraction $\frac{x}{x+2\alpha}$ approaches $\frac{x}{x} = 1$, and the normal course is restored. The greater therefore α , the longer the almost horizontal course will maintain itself in the neighbourhood of T_0 .

If α absolute $= 0$, then $\frac{x}{x+2\alpha(1-x)}$ may be replaced by $\frac{x}{x} = 1$ from the beginning, and we have *immediately* the normal course, given by

$$\frac{dT}{dx} = -\frac{1}{1-x} \frac{RT^2}{q},$$

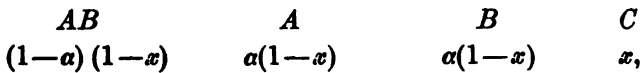
yielding:

$$\left(\frac{dT}{dx}\right)_0 = -\frac{RT_0^2}{q}.$$

Also T_0 and T_{ab} then coincide.

5. In fig. 1 also the line T_0B has been drawn. This would be the melting-point line, when instead of an excess of one of the products of dissociation, an excess of an indifferent substance C was added.

The equation (5) remains then the same. But now (6) becomes different. We have now namely:



together again $1 + \alpha(1-x)$ molecules.

Hence the dissociation isotherm becomes:

$$\frac{\alpha(1-x)}{N} \times \frac{\alpha(1-x)}{N} : \frac{(1-\alpha)(1-x)}{N} = K,$$

or

$$\frac{\alpha^2}{1-\alpha} \frac{1-x}{1+\alpha(1-x)} = K \quad . \quad . \quad . \quad . \quad . \quad (10)$$

Now α does not decrease with x , but increase. The added indifferent substance C may viz. be considered as "diluent", whereas in the preceding question the addition of one of the products of dissociation depresses the degree of dissociation α .

If we solve from (10) again α , we find in this case:

$$\alpha^2(1-x) + \frac{K}{1+K} \alpha x - \frac{K}{1+K} = 0.$$

By putting $x=0$, it appears again that $\frac{K}{1+K} = \alpha_0^2$, so that we must solve α from

$$\alpha^2(1-x) + \alpha_0^2 \alpha x - \alpha_0^2 = 0,$$

in which α_0 is again provisionally assumed to be independent of T . (Cf. § 3).

Now we find:

$$\alpha = \alpha_0 \left[-\frac{1}{2}\alpha_0 x + \sqrt{\frac{1}{4}\alpha_0^2 x^2 + (1-x)} \right] : (1-x),$$

so

$$\left. \begin{aligned} (1-\alpha)(1-x) &= (1-x) - \alpha_0 \left[-\frac{1}{2}\alpha_0 x + \sqrt{\frac{1}{4}\alpha_0^2 x^2 + (1-x)} \right] \\ 1 + \alpha(1-x) &= 1 + \alpha_0 \left[-\frac{1}{2}\alpha_0 x + \sqrt{\frac{1}{4}\alpha_0^2 x^2 + (1-x)} \right] \end{aligned} \right\}.$$

The quantity occurring in (5) under the sign \log becomes then:

$$\frac{(1-x) + \frac{1}{2}\alpha_0^2 x - \alpha_0 \sqrt{\frac{1}{4}\alpha_0^2 x^2 + (1-x)}}{1 - \frac{1}{2}\alpha_0^2 x + \alpha_0 \sqrt{\frac{1}{4}\alpha_0^2 x^2 + (1-x)}}.$$

Now $\sqrt{\frac{1}{4}\alpha_0^2 x^2 + (1-x)} = 1 - \frac{1}{2}\alpha_0^2 x + \frac{1}{8}\alpha_0^4 x^2 - \frac{1}{16}\alpha_0^6 x^3 + \dots$, so that the above fraction passes into

$$\frac{1 - \alpha_0 - \frac{1}{2}\alpha_0(1-\alpha_0)(2+\alpha_0)x + \frac{1}{8}\alpha_0(1-\alpha_0^2)x^2 \dots}{1 + \alpha_0 - \frac{1}{2}\alpha_0(1+\alpha_0)x - \frac{1}{8}\alpha_0(1-\alpha_0^2)x^2 \dots}$$

i. e. into

$$\frac{(1-\alpha_0)[1 - \frac{1}{2}\alpha_0(2+\alpha_0)x + \frac{1}{8}\alpha_0(1+\alpha_0)x^2 \dots]}{(1+\alpha_0)[1 - \frac{1}{2}\alpha_0 x - \frac{1}{8}\alpha_0(1-\alpha_0)x^2 \dots]}$$

or into

$$\frac{1-\alpha_0}{1+\alpha_0} [1 - x - \frac{1}{4}\alpha_0 x^2 \dots].$$

Owing to this we get:

$$-\log [1 - x - \frac{1}{4}\alpha_0 x^2 \dots] = \frac{q}{R} \left(\frac{1}{T} - \frac{1}{T_0} \right),$$

or

$$x + \frac{1}{4}(2 + \alpha_0)x^2 = \frac{q}{R} \left(\frac{1}{T} - \frac{1}{T_0} \right),$$

or finally, substituting, $Q_0 = q + \alpha_0 \lambda$ for q (cf. § 3), and $T_0 = \left(1 - \frac{RT_0}{Q_0} x\right)$ for TT_0 :

$$T_0 - T = \frac{RT_0^2}{Q_0} \left[x + \frac{1}{4} \left(1 + \frac{1}{4} \alpha_0 - \frac{2RT_0}{Q_0} x \right) x^2 \right], \quad (5b)$$

which approximate expression will now at least hold for values of $x < 0.26$.

6. A general expression for $\frac{dT}{dx}$ in the case in question may be most conveniently calculated from (4). (cf. § 4). Then we get:

$$\frac{dT}{dx} = \frac{RT^2 \frac{d \log c_0}{dx}}{Q},$$

where

$$\begin{aligned} \frac{d \log c_0}{dx} &= \frac{\partial \log c_0}{\partial x} + \frac{\partial \log c_0}{\partial \alpha} \frac{d\alpha}{dx} = \\ &= -\frac{1}{(1-x)(1+\alpha(1-x))} - \frac{2-x}{(1-\alpha)(1+\alpha(1-x))} \frac{d\alpha}{dx}. \end{aligned}$$

But now $\frac{d\alpha}{dx}$ is different. From (6^a) we find viz.:

$$\frac{2}{\alpha} \frac{d\alpha}{dx} + \frac{1}{1-\alpha} \frac{d\alpha}{dx} - \frac{1}{1-x} - \frac{1}{1+\alpha(1-x)} \left\{ -\alpha + (1-x) \frac{d\alpha}{dx} \right\} = 0,$$

yielding:

$$\frac{d\alpha}{dx} = \frac{\alpha(1-\alpha)}{(1-x)(2-\alpha x)},$$

so no longer negative, but positive as it should be (see above). After substitution we get:

$$\begin{aligned} \frac{d \log c_0}{dx} &= -\frac{1}{(1-x)(1+\alpha(1-x))} - \frac{\alpha(2-x)}{(1-x)(2-\alpha x)(1+\alpha(1-x))} = \\ &= -\frac{2}{(1-x)(2-\alpha x)}, \end{aligned}$$

so that we find :

$$\frac{dT}{dx} = - \frac{RT^*}{Q} \frac{1}{1-x} \frac{2}{2-\alpha x} \dots \dots \dots (11)$$

In this Q is again $= q + \alpha \lambda - x(1-x) \frac{d\alpha}{dx} \lambda$. After substitution of the just found value for $\frac{d\alpha}{dx}$, this becomes :

$$Q = q + \alpha \frac{2-x}{2-\alpha x} \lambda \dots \dots \dots (12)$$

For $x=0$ (11) becomes now :

$$\left(\frac{dT}{dx} \right)_0 = - \frac{RT_0^*}{Q_0} = - \frac{RT_0^*}{q + \alpha_0 \lambda} \dots \dots \dots (11a)$$

So the melting-point curve has now also at $T=T_0$ a perfectly normal course.

For *practical* purposes we can determine more or less accurately the value of α_0 from the approximate equation (5a) (for small values of x), which according to (7) renders also an estimation of T_{ab} possible. The value of Q_0 must then of course be known. It can, however, also be calculated from the accurate determination of the initial course of T, B (with indifferent admixture), according to equation (11a).

If we then determine $\frac{dT}{dx}$ once more for that same line for $x=0,1$ or $0,2$ e.g., we can find Q by means of (11), i.e.

$$q + \alpha \lambda - \alpha \lambda \frac{(1-\alpha) x}{2-\alpha x},$$

supposing that we may put $\alpha = \alpha_0$ by first approximation. We find then by subtraction of the above found value of $q + \alpha_0 \lambda$ the value of $\alpha_0 \lambda \frac{(1-\alpha_0) x}{2-\alpha_0 x}$, so that of λ separately. Also q is then separately known.

Appendix. The approximate equations (5a) and (5b) might also have been derived from :

$$T = T_0 + x \left(\frac{dT}{dx} \right)_0 + \frac{1}{2} x^2 \left(\frac{d^2 T}{dx^2} \right)_0 + \frac{1}{6} x^3 \left(\frac{d^3 T}{dx^3} \right)_0 + \dots$$

With (5a) we find then easily from the value (8) for $\frac{dT}{dx}$, that

$$\left(\frac{dT}{dx}\right)_0 = 0; \left(\frac{d^2T}{dx^2}\right)_0 = \left(\frac{1}{x_0} + \frac{3}{2}\right)\left(\frac{dT}{dx}\right)_0 = \frac{1}{x_0}\left(\frac{dT}{dx}\right)_0 = -\frac{RT_0}{Q_0} \frac{1}{2\alpha_0};$$

and $\left(\frac{d^3T}{dx^3}\right)_0 = \frac{3}{x_0}\left(\frac{dT}{dx}\right)_0$. In this it is noteworthy, that on account of

$$Q = q + \left[\alpha - x(1-x)\frac{d\alpha}{dx}\right] \text{ also } \left(\frac{dQ}{dx}\right)_0 = 0.$$

With (5^b) we shall find from (11): $\left(\frac{dT}{dx}\right)_0 = -\frac{RT_0}{Q_0}; \left(\frac{d^2T}{dx^2}\right)_0 =$

$$= \left(1 + \frac{1}{2}\alpha_0 - \frac{2RT_0}{Q_0}\right)\left(\frac{dT}{dx}\right)_0. \text{ Here too } \left(\frac{dQ}{dx}\right)_0 = 0.$$

Chemistry. — “On ocimene and myrcene, a contribution to the knowledge of the aliphatic terpenes.” By Dr. C. J. ENKLAAR. (Communicated by Prof. P. VAN ROMBURGH).

(Communicated in the meeting of Januari 27, 1906).

The aliphatic terpene group, discovered in 1890 by SEMMLER¹⁾, is characterised by the absence of closed rings; the terpenes of this group possess, therefore, three double links in an open chain. The first aliphatic terpene described was anhydro-geraniol, which SEMMLER prepared²⁾ from the aliphatic terpene alcohol geraniol by heating the same with potassium hydrosulphate. This terpene has not yet been obtained pure, and has been but little investigated. A naturally occurring terpene of this group was found by POWER and KLEBER³⁾ in oil of Bay (the ethereal oil of *Myrcia acris* D. C.); it was called by them myrcene. The sp. gr. (0,801 at 15°) was much lower than that of the cyclic terpenes (0,840—0,860), the molecular refraction and the addition of bromine pointed to the presence of three double links. With permanganate myrcene yielded some succinic acid, on treatment with mixed sulphuric and glacial acetic acid an alcohol was obtained, having the odour of oil of bergamotte, which was taken for linalool on account of its oxidation to citral. Myrcene oxidised in contact with the air, and polymerised even at the ordinary temperature. In his studies on caoutchouc HARRIES⁴⁾ has for some time considered these polymerisation products as closely allied or iden-

¹⁾ Ber. **23**, 2965 (1890), and **24**, 201 and 682 (1891).

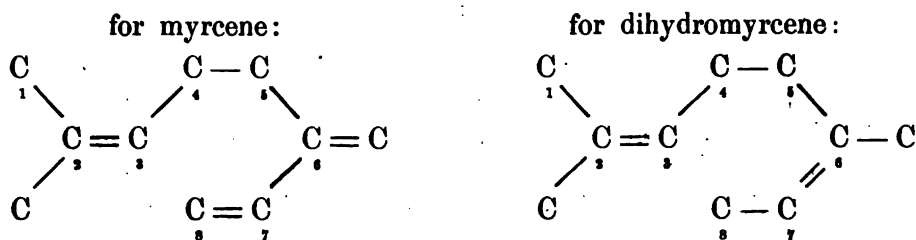
²⁾ Ber. **24**, 682 (1891).

³⁾ Pharm. Rundschau (New-York) **1895**, no. 18.

⁴⁾ Ber. **35**, 3256 (1902).

tical with caoutchouc, on account of similar nitrites being formed from them.

On treatment with sodium and alcohol, SEMMLER¹⁾ obtained from myrcene a dihydromyrcene, which induced him to suppose the presence in myrcene of a conjugate system of double links. In connection with the formation of succinic acid from myrcene, and of laevulinic acid from dihydromyrcene, he constructed the following formulae :



For a long time, myrcene remained the only known naturally occurring aliphatic terpene. CHAPMAN²⁾ also found it in the oil of hops, POWER and KLEBER³⁾ rendered its presence probable in the ethereal oil from the leaves of the Sassafras tree, BARBIER⁴⁾ in the ethereal oil of *Lippia citriodora*. At Buitenzorg, however, VAN ROMBURGH⁵⁾ found that the leaves of a variety (sub-variety) of *Ocimum Basilicum* L. contained an ethereal oil, in which occurred a still unknown aliphatic terpene which he called ocimene. Apart from its odour it was distinguished from myrcene by a greater index of refraction, a more powerful absorption of oxygen, and by the peculiarity of passing into an isomer at its boiling point at the ordinary pressure. The molecular refraction of ocimene gave a considerably higher value than the calculated value for $\text{C}_{10}\text{H}_{16}$, so that the proof of the aliphatic character of ocimene was, as yet, wanting.

The further investigation of ocimene was yielded to me by Prof. VAN ROMBURGH; the ocimene formed the subject of my dissertation⁶⁾. My research, which at first concerned only ocimene, had soon to be extended to the aliphatic terpenes in general, particularly to myrcene and the isomer formed from ocimene.

¹⁾ Ber. **34**, 3122 (1901).

²⁾ Journ. of the Chem. Soc. Trans. **67**, 54 (1895) and **83**, 505 (1908).

³⁾ Pharm. Review **1896**, Chem. Centr. Bl. **1897**, II, 42.

⁴⁾ Bull. Soc. Chim. [3], **25**, 691 (1901).

⁵⁾ Verslagen van 's Lands Plantentuin te Buitenzorg, 1899, p. 48, and These Proc. III. p. 454.

⁶⁾ C. J. ENKLAAR, „Over ocimeen en myrceen, eene bijdrage tot de kennis van de aliphatische terpenen”. Acad. proefschrift, Utrecht, Dec. 1905. A more extended communication will appear in the Rec. des Trav. d. chim. des Pays-Bas.

The three aliphatic terpenes investigated by me (the isomer of ocimene proved later on to be also an aliphatic terpene) form together a closely related, natural group which, according to my structural formulae, embraces the dehydration products of the terpene alcohol, linalool, which occurs so widely in the vegetable kingdom. The ocimene obtained by distillation in vacuo over metallic sodium is an optically inactive liquid of an agreeable ester-like odour, which possesses the following constants :

sp. gr.,	nd.,	b.p. at 30 mM.	b.p. at ordinary pressure.
0,8031	1,4857	81°	172°,5.

Whilst it boils constantly at diminished pressure, the boiling point at the ordinary pressure does not remain constant for a minute, and after 25 minutes the original product is found to be nearly wholly converted into an isomer, which boils 17° higher than ocimene. By fractionation in vacuo it may be obtained pure, and it then possesses the following constants ¹⁾ :

sp. gr.,	nd.	b.p. at 12 mM.	b.p. at 750 mM.
0,8182	1,5296	81°	188°.

The myrcene was partly prepared by myself from the oil of Bay, for another part I used a myrcene, most willingly held at my disposal by the firm of SCHIMMEL and Co. In accordance with others, I found for the myrcene the following constants :

sp. gr.,	nd.,	b.p. at 760 mM.
0,8013	1,4700	166°

At the ordinary temperature these terpenes are stable, except myrcene, which then undergoes a slow polymerisation; the isomer of ocimene is pretty soon altered in strong daylight. The chemical reagents which can be absorbed by unsaturated compounds are readily taken up by these terpenes. Up to the present, however it has not been possible to isolate well-defined additive products, with the exception of the compound formed from myrcene and hydrogen. Crystallised derivatives of these terpenes are as yet quite unknown, which very much impedes their detection in ethereal oils and their investigation. If the chemistry of the aliphatic terpenes is not to experience the same fate as that of the cyclic terpenes before WALLACH's researches, it now becomes all important, to devise a further characteristic, based, if possible, on crystallised derivatives. The following

¹⁾ This change of ocimene into an isomer has been noticed and already communicated by VAN ROMBURGH (l.c.). The constants I found agree with those previously observed by him. I followed his directions for the preparation of ocimene from the ethereal oil.

contains a description of some derivatives obtained from the terpenes ocimene and myrcene; from ocimene and myrcene a crystallised dihydrotetrabromide (m. p. 88°), from ocimene a phenylurethane (m. p. 72°) from the new terpene alcohol ocimenol, obtained from ocimene, from myrcene a phenylurethane (m. p. 68°) from the corresponding terpene alcohol, myrcenol, which had not yet been recognised as a new product.

As will be shown, the preparation of these crystallised derivatives enabled me to confirm with certainty certain facts already surmised and to find a few new ones of great importance for the further research.

As regards the additive experiments, it may be mentioned, that in the bromination the final point is difficult to observe on account of colorations; in the case of both ocimene and its isomer the quantity absorbed seemed to point to the presence of three double links. Of some more importance is the behaviour of these substances towards oxygen. With some other unsaturated hydrocarbons they share the property of absorbing oxygen. The isomer of ocimene does this in a very striking manner. When a glass plate is moistened with this liquid, it is found to be changed after half an hour into a film or resinous crust. Ocimene does this also very strongly, myrcene a little less. The final point of the absorption seems to be reached after the fixation of two atoms of oxygen¹⁾.

I have specially investigated the behaviour of ocimene towards permanganate. There is no question here of the isolation of glycols such as WAGNER has obtained from many unsaturated substances. Even should a glycol be formed with a same number of carbon atoms as ocimene, this is very rapidly oxidised by the permanganate. As oxidation products are formed in large quantities carbonic acid, acetic acid, oxalic acid, acetone and a small portion of higher fatty acids, also traces of some non-volatile acids, among which is perhaps pyruvic acid. In a very weak solution of acetone, the oxidation takes place more moderately. After the absorption of 9 atoms of oxygen the discoloration of the permanganate ceases; according to my determinations 25 % of the ocimene is then oxidised to carbon dioxide. The greater part of the oxidation products is, however, volatile with the acetone; a very small quantity of a sirupy glycol gave on oxidation with hydrogenperoxide a little carbonic acid, acetone, acetic acid and in addition a fair amount of a non-volatile acid, which is probably malonic acid. It is remarkable, however,

¹⁾ In connection with the researches of ENGLER on the oxygen absorption of the fulvenes and of WALLACH on that of phellandrene, I hope to further investigate this matter.

that in the oxidation in acetone solution no acids higher than acetic acid were formed and besides not a trace of oxalic acid with hydrogen-peroxide. I am therefore of opinion that those substances owe their origin to migration of double links during the oxidation. All this causes that, I, for one, consider the structural formulae based on oxidation experiments with such very changeable substances as very untrustworthy. One should also be very careful in drawing conclusions from the isolation of small quantities of the more typical decomposition products, as these may have been yielded by impurities.

Notwithstanding the beautiful researches of TIEMANN and SEMMLER ¹⁾ on geranial, citral, etc, the structural formulae of none of the members of the aliphatic terpene group seems to have been sufficiently established as was only recently shown by HARRIES oxidations with ozone ²⁾.

Meanwhile I had tried, whether ocimene could be hydrogenised like myrcene by means of sodium and alcohol. This proved to be the case. Ocimene, therefore, also contains a conjugate system of double links. The hydro-product, which I obtained, had the composition $C_{10}H_{18}$ ³⁾ (I will call it in future dihydro-ocimene); it is a very mobile liquid of an agreeable odour. For its constants I found the following values :

sp. gr. ₁₁	nd. ₁₇	b.p. at 761 mm.
0,7792	1,4507	166°—168°

whilst SEMMLER ⁴⁾ states for dihydromyrcene :

sp. gr.	nd.	b.p.
0,7802	1,4501	171°,5—172°,5.

The temperature, at which the specific gravity was determined, and the barometric pressure at the boiling point are not stated ; at 770 mM., the boiling point of dihydro-ocimene is, however, but little higher. Owing to this difference of 6° in the boiling point of

¹⁾ Ber. 28, 2126 (1895).

²⁾ Ber. 36, 1933, 2998, 3001, 3658; and 37, 612, 839, also HARRIES und SCHAUWECKER, Ber. 34, 2987 (1901) and HARRIES, Lehrbuch der Org. Chem. by V. MEYER und P. JACOBSON, II, 754. The above-standing was written before the latest publication of HARRIES on this subject appeared (Lieb. Ann. Jan. 1906).

³⁾ In the combustion of these substances with copper oxide in an open tube the carbon is often found a good deal too low, but in the closed tube with lead chromate the exact values are always obtained. On the strength of his analyses, CHAPMAN also concluded at first to the presence in oil of hops of a hydrocarbon $C_{10}H_{18}$ which by further investigation proved to be myrcene.

⁴⁾ l. c.

the said hydrocarbons, these were not considered as identical in the provisional communication. A second point of difference was the obtainment of a crystalline bromide from dihydro-ocimene. When, afterwards, I repeated SEMMLER's experiments, I found the boiling point of dihydromyrcene to be the same as that of dihydro-ocimene, whilst the other constants (as far as could be ascertained) agreed with those of SEMMLER; I found the following values:

sp. gr. ₁₆	nd. ₁₇	b.p. at 761 mm.
0,7852	1,4514	166°—168°

Like SEMMLER, I found that myrcene and its hydro-product have the same boiling point so that, probably, SEMMLER's statement is based on a mistake; for other investigators also state 166° as being the boiling point of myrcene.

The now probable identity of the hydro-products became a certainty by the bromination of dihydromyrcene. As stated, dihydro-ocimene had given me on bromination a crystalline bromide; from the oil obtained at first, it crystallises to the extent of 12—14%. After repeated crystallisations from methyl alcohol it forms snow-white crystals which melt, sharply, at 88°. Analysis and determination of molecular weight pointed to the composition $C_{10}H_{16}Br_4$. In most of the organic solvents, this bromide is readily soluble, but in methyl alcohol only to the extent of 1,2%; on boiling with sodium hydroxide and also with silver oxide and water an oil smelling of peppermint is obtained. From dihydromyrcene I now obtained the same bromide. The oil obtained by SEMMLER soon solidifies when, after being purified, it is put away to crystallise in a cool place; by applying a little artifice I succeeded in instantly inducing the crystallisation. The identity was proved by the fact that this bromide like all its mixtures with dihydro-ocimenetetrabromide, melted, sharply, at 88° and also that the solubility of dihydro-ocimenebromide was practically not affected by addition of this substance.

This now completely proves:

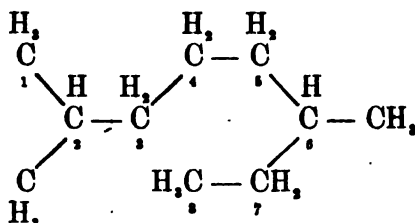
1. that both ocimene and myrcene are aliphatic terpenes.
2. that the dihydroproducts of these terpenes are identical.

From this it follows — and this is probably of more importance still — that we may now deduce the structural formulae of ocimene and myrcene from the obtained data.

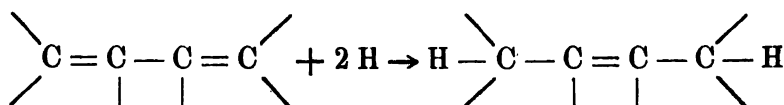
As regards myrcene, owing to its connection with citral and dipentene¹⁾, it was already fairly certain that, like all aliphatic

¹⁾ POWER and KLEBER, l. c.

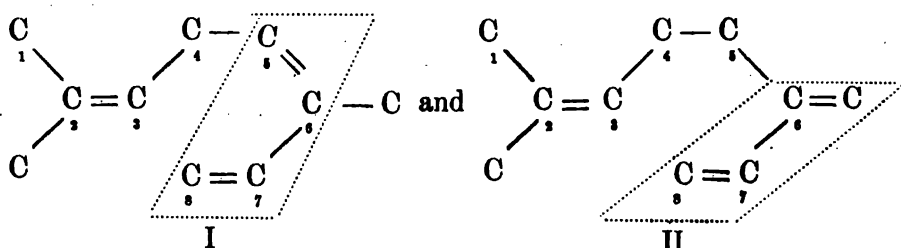
terpenederivatives as yet known, it is a derivative of dimethyl-2-6 octane :



On account of the proved identity of the bromides, ocimene should also possess this carbon skeleton. Now when we accept the correctness of the hydrogenation principle of conjugate systems ¹⁾:



it is, in the carbon branch formation of dimethyl 2—6-octane, only then possible for different trienes to give identical dienes, when these trienes possess the following conjugate systems :

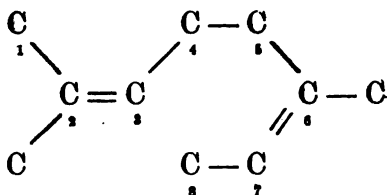


and when the third double link occupies the same position in both formulae, and is not conjugate with the other double links. For this third double link 1 or 2 is the only possible position ; on account of my experiences as to the oxidation of ocimene, I should be inclined to accept the position 2, although the position 1 has still quite as much right of existence²⁾. Perhaps, as SEMMLER believes, myrcene may contain both forms (ortho and pseudo form).

Dihydro-ocimene and dihydromyrcene then assume the formula of dimethyl 2—6 octadiene 2—6 :

¹⁾ For exact details and the literature of this hydrogenation principle, I must refer to my dissertation p. 26. I wish only to point out particularly, that my rule is not based on the theory of THIELE; but has been deduced in a purely empirical manner. I, therefore, make a distinction between the addition of hydrogen and that of other substances which may prove more complicated.

²⁾ Admitting for this third double link the position I, yet another couple of formulae seems possible; on account of other facts the latter must however be rejected.



which has already been agreed to by SEMMLER on other grounds. Which of the above formulae, however, belongs to ocimene and which to myrcene? A choice is only possible on the strength of other data. As has been stated, SEMMLER had assigned to myrcene formula II on account of the formation of succinic acid in the oxidation. Independently of him and these considerations, I had constructed for ocimene formula I as the result of my oxidation experiments, but without attaching any value to this. A closer consideration of the above formulae, coupled with the peculiar behaviour of ocimene on heating, as observed by VAN ROMBURGH, led me to the discovery of a fact, which rendered a choice possible with great certainty.

In one respect formula I differs characteristically from formula II namely by the presence of the double link 5, which forms an asymmetric system with the carbon atoms combined thereby and the groups attached thereto, and so gives an opportunity for the existence of a geometric isomerism. The transformation of ocimene into its isomer led me to think that these two substances might be geometrically (stereo-) isomeric. Geometrical isomers are often readily converted into each other on warming; for instance, WISLIZENUS noticed the transformation of the one bromobutylene into the other on distillation. The hypothesis advanced by me was easy to verify for on hydrogenation the same dihydro-ocimene ought to be formed from the isomer as from the ocimene itself. This proved indeed to be the case. The physical constants of these materials were indeed identical as is shown from the following table:

	sp. gr. ₁₅	nd. ₁₇	b.p. at 761 mm.
dihydro-ocimene	0,7792	1,4507	166°—168°
dihydro-isomere	0,7793	1,4516	167°—168°

whilst the original products exhibit strong differences as is shown from the subjoined ¹⁾:

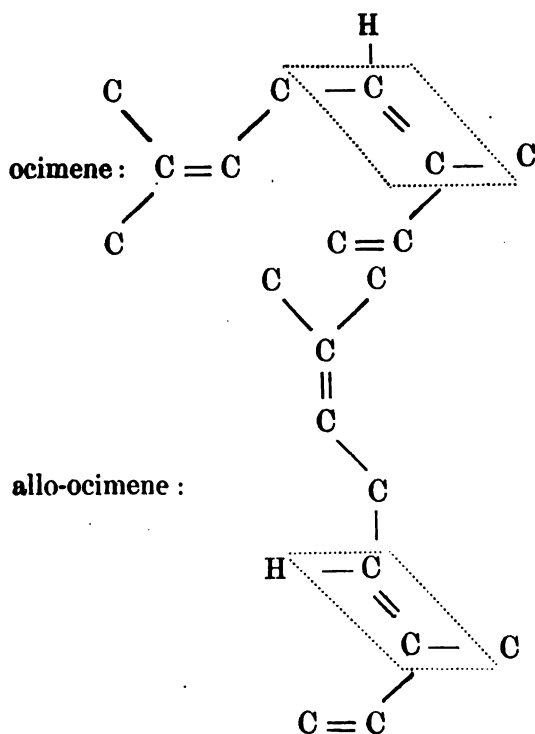
	sp. gr. ₁₅	nd.	b.p. at 760 mm.
ocimene	0,8031	1,4857	172°,5
isomer	0,8133	1,5447	188°

¹⁾ The constants of the isomer have been determined with the aid of a purer preparation than those previously communicated. On heating ocimene some by-products seem to be formed.

With this I consider the identity of these hydro-products and the geometrical isomerism of the terpenes as proved. The isomer of ocimene I will call in future allo-ocimene. It is remarkable that allo-ocimene deviates 6,31 from the theory of BRÜHL; its index of refraction is also greater than that of the hydrocarbon and it has also a strong dispersion power. This, as BRÜHL thinks ¹⁾, is perhaps connected with the presence of a conjugate system of double links. Provisionally, one should be careful in drawing conclusions as other substances also exhibit such differences. Allo-ocimene is, however, in this respect a unicum in organic chemistry. Dihydro-ocimene on the other hand exhibits the correct refraction. The deduced geometrically isomerism was also very much supported by the behaviour of the isomer towards a mixture of sulphuric and glacial acetic acid. Whilst ocimene remains for the greater part unchanged and is, to a small extent, converted into an alcohol, allo-ocimene is for the greater part converted into a polymerisation product, whilst there is left a small quantity of terpene, which proved to be nothing else but ocimene. This typical difference between the two ocimenes is perhaps connected with the particular tension which the ethylene link may attain here. Possibly, at the moment this ethylene link opens, the two connected atoms of three molecules combine to form a cycle of six atoms; a substituted hexa-hydrobenzene derivative would then be formed; the polymerisation product would be this triterpene.

The regeneration of ocimene from allo-ocimene under the influence of dilute acids renders the analogy complete with the isomerism of fumaric and maleinic acid. After what has been said, it is no longer doubtful, that ocimene, which possesses the double link 5, is represented by formula I, whilst myrcene is represented by formula II, which has now been deduced independently of the results of the oxidation. But few instances of geometrical isomerism have been noticed with hydrocarbons and this is the first known in the terpene series. It seems to me not impossible that the absence of the cyclic link has given nature the opportunity of forming a labile geometrical isomer; it is remarkable, however, that this has taken place without any admixture of allo-ocimene. I hesitate to pronounce just now an opinion as to the nature of that geometrical isomerism with ocimene and allo-ocimene; the following projection formulae seem to me the most probable.

¹⁾ Ber. 88, 761 (1905).



I am still engaged with this geometrical isomerism and the other substances described. I soon hope to make a further communication about the alcohols formed from these terpenes.

Of late, after this research had already been partly finished, SABATIER and SENDE-RENS have made some valuable additions to our methods of research of the unsaturated compounds. I am engaged in applying the same to the aliphatic terpene group and to the sesquiterpenes. Dihydro-ocimene, which cannot be further hydrogenised by sodium and alcohol, eagerly absorbs hydrogen at 180°

under the influence of reduced nickel; a nearly odourless liquid is formed which boils at a considerably lower temperature and contains only traces of the original product. It consists, probably, of dimethyl-2.6.octane, the as yet unknown foundation of the aliphatic terpene group. The aliphatic terpene-alcohol, geraniol, also reacts with nickel and hydrogen; the reaction product is a liquid, possessing a particular odour; it contains, besides some water, a hydrocarbon, which probably is identical with the hydrocarbon, obtained from dihydroacimene and a substance of a higher boiling point, which I suppose to be the saturated alcohol, corresponding with geraniol.

Chemistry. — “*On some aliphatic terpene alcohols.*” By DR. C. J. ENKLAAR. (Communicated by Prof. P. VAN ROMBURGH).

(Communicated in the meeting of January 27, 1906).

According to the process of BERTRAM and WALBAUM¹⁾ terpene alcohols may be obtained from terpenes by digesting their solution in glacial acetic acid for some hours with dilute sulphuric acid at 50°—60°. The aliphatic terpene ocimene, discovered by VAN ROMBURGH

¹⁾ D. R. Pat. No. 80711, Journ. f. Prakt. Chem. 49. 1. Also compare WALLACE and WALKER, Ann. 271, 285, and POWER and KLEBER, Pharm. Rundschau (N.-York) 1895, No. 3.

and investigated by myself¹⁾, was treated by me in this way²⁾. The greater half of the ocimene operated upon was recovered unaltered while a small portion underwent polymerisation. At the same time an alcohol was formed, the quantity of which was about 10% of the ocimene used. This alcohol was an agreeably smelling liquid, which gave the following constants:

sp. gr.,	nd.,	B.p. at 10 mm.	Mol. Refraction (M.R.)
0.901	1.4900	97°	49.22

(calculated for $C_{15}H_{18}O$ is: MR = 48.86)

The analysis had given the composition $C_{15}H_{18}O$.

This alcohol, probably an aliphatic terpene alcohol is, therefore, formed by the addition of the elements of water to ocimene. In properties it does not correspond with any of the already known aliphatic terpene alcohols, as is shown by the following table:

	sp. gr.,	nd	B.p. at 10 mm.
geraniol:	0,882	1.477	116°
nerol ³⁾ :	0,8814		112°
myrcenol (BARBIER):	0,901	1.477	99°
linaloöl:	0,870	1,464	86°

On account of its formation from ocimene, I call this new alcohol ocimenol. The investigation of this ocimenol is still of a provisional character.

The beautifully crystallised phenylurethane, which I could prepare from it in good yield, renders it possible to characterise and readily investigate the alcohol. This urethane, when recrystallised from dilute alcohol, forms white needle-shaped crystals, which melt without decomposition at 72°, whilst according to the analysis, it has the composition $C_{17}H_{22}O_2N$. I am still occupied with the regeneration of ocimenol from its urethane and the closer investigation of these substances; however from the fair yield of this urethane, and the absence of oily by-products, it seems that the product obtained from ocimene is mainly a simple alcohol.

For me, the study of this alcohol was of particular importance as I wanted to compare ocimene in this respect with myrcene. Several investigators have been already occupied with the alcohol,

¹⁾ Compare my previous paper and my dissertation.

²⁾ I worked according to the directions of POWER and KLEBER. 100 parts of terpene were heated with 250 parts of glacial acetic acid and 10 parts of 50% sulphuric acid for three hours at 40°.

³⁾ Nerel is distinguished from geraniol by a more delicate odour of roses, by not combining with calcium chloride and by yielding a diphenylurethane melting at 52°.

which is formed from myrcene in the manner indicated; their statements, however, are often diametrically opposed.

POWER and KLEBER¹⁾, who first prepared it, took it to be linaloöl on account of its odour and the formation of citral on oxidation with chromic acid. BARBIER²⁾ declared it to be a new alcohol; on oxidation, he obtained no citral but another as yet unknown aldehyde. From the results of the oxidations he deduced for this alcohol, which he named myrcenol, a structural formula, which had been given already by TIEMANN and SEMMLER to linaloöl. In a further research on linaloöl, he gave as his opinion³⁾ that it was not a simple alcohol, but a mixture, and also that its main constituent was not optically active, a reason why he rejected the formula of T. and S. SEMMLER⁴⁾, however, looked upon myrcenol as a mixture already partly converted into cyclic products, and upheld his linaloöl formula against BARBIER's objections.

I prepared the myrcenol according to the directions of POWER and KLEBER. The greater part of the myrcene was recovered unaltered (6%), a small portion polymerised whilst the alcohol had formed to the amount of about 20%. For this alcohol distinguished from linaloöl also by its intense, agreeable odour, I obtained the constants attributed to it by BARBIER, who, however, had a much larger quantity of the alcohol at his disposal:

	sp. gr.,	nd_{11} ,	Bp. at 10 mM.	Mol. Refr.
myrcenol (<i>E</i>):	0,9032	1.4806	97—99°	48,44
„ (<i>B</i>):	0,9012	1.47787	99°	48,34

MR, calculated for $C_{11}H_{18}O$ = 48,16

My analyses also pointed to the composition $C_{11}H_{18}O$. I do not consider this alcohol to be perfectly pure as it has not got a quite constant boiling point; it seems still to contain a more volatile fraction.

The closer investigation of this substance has, as stated, led to differences of opinion. It seems to me that these have been caused by the different methods used. The formation of citral in the oxidation in acid solution is no reliable test for the presence of linaloöl as it may be yielded also by other alcohols. BARBIER showed, however, that on oxidation of myrcenol with chromic acid an aldehyde was formed, having the same formula as citral, but not identical with the same. He regenerated it, for instance, from its oxime, and obtained a

¹⁾ l. c.

²⁾ Bull. Soc. Chem. [3], 25, 687 (1901).

³⁾ Bull. Soc. Chem. [3], 25, 828 (1901).

⁴⁾ Ber. 34, 3122 (1901).

semicarbazone melting at 197° , whilst citralsemicarbazone melts at 135° . Here we have a difference in the method of research. POWER and KLEBER tested for citral by converting it into citrylnaphthocinchonic acid; in this way a possibly formed ketone — I presume myrcenol is a secondary alcohol — must have escaped their notice, whilst a little citral thus detected may be simply a by-product. On the other hand, semicarbazone, made use of by BARBIER, is according to others unfit for testing for citral. BARBIER may have obtained the semicarbazone from the eventually formed ketone, the main product, whilst a little admixed citral may have given the aldehyde reactions. Moreover BARBIER's oxidations with permanganate in aqueous solutions cannot be taken as decisive for the differentiation of myrcenol and linalool ¹⁾.

Instead of investigating the oxidation products of myrcenol, I have prepared from the alcohol itself a crystallised derivative, in the form of a phenyl-urethane, melting at 68° . The analysis again pointed to the composition $C_{11}H_{18}O_2N$. This urethane has been prepared in the same manner as WALBAUM and HÜTHIG ²⁾ prepared the phenyl-urethane from linalool; the latter melts at 65° . By means of the phenyl-urethane obtained from myrcenol, it could be decided very readily and distinctly, that the alcohols, myrcenol and linalool, were totally different. The mixture of racemic linaloolurethane and myrcenol-urethane melted at 60° — 62° ; the depression of the melting point sufficiently proves the non-identity. The alcohol, which is characterised by the phenyl-urethane melting at 68° , is also the main product of crude myrcenol. I obtained from this a yield of nearly 60 pCt. of crystallised urethane; besides this alcohol, a little linalool may possibly be contained in the myrcenol (the hydration product of myrcene); the formation of some oily urethane in presence of the crystallised substance might even point to this. The facts mentioned render it possible, however, to decide the matter. By regenerating myrcenol from its urethane, the properties of pure myrcenol may be ascertained. I am still engaged with this. Of this alcohol, myrcenol, it may be stated that it is a typical derivative of myrcene; its constants differ from those of ocimenol, in the same manner as those of myrcene do from those of ocimene; the tendency towards polymerisation of myrcenol is still larger than that of myrcene.

For ocimenol and myrcenol I devised provisional structural formulae³⁾, based on their formation from the terpenes ocimene and myrcene.

¹⁾ Compare previous communication.

²⁾ Journ. f. prakt. Chem. **67**, 323 (1903).

³⁾ Dissertation, p. 78.

I have not been able to obtain the above racemic urethane of linaloöl by mixing *d*- and *l*-linaloöl and preparing the urethane from this racemic linaloöl; nothing but an oil was formed, which could not be brought to crystallise. Still, from each oil separately (*d*-coriandrol and *l*-linaloöl, the latter obtained from SCHIMMEL & Co.) I obtained the urethanes at once crystalline. In order to obtain racemic urethane, I was obliged to mix these urethanes of *d*- and *l*-linaloöl in the proportion of their optical activity. The latter, however, had not been determined; in fact it was doubtful whether they were optically active at all. WALBAUM and HÜTHIG, who desired to prove in this manner the identity of linaloöl derived from different ethereal oils, have overlooked the fact, that alcohols of such varying optical activity as those found with linaloöl (from 1° to 35°) could not yield the same phenyl-urethane.

Racemic urethane has generally quite another melting point than the pure optically active substance. I was, therefore, obliged to fill this void in their research. I found that the yield of crystallised urethane, which only amounts to 15%, when one works according to their directions (time of reaction one week), may be increased to 85% increase of the time to three months. The urethanes formed, which all melt at 65° are optically active in proportion with the optical activity of the alcohols started from. They consist of mixtures of racemic urethane (probably a racemic compound) with the optically active component, which in a pure condition shows a rotation of $23^{\circ} 27'$ in a 200 mM. tube and has the m.p. 66° . The rotation of pure optically active linaloöl under the same conditions may also be calculated from this; it then becomes $35^{\circ} 27'$, whereas the highest observed rotation of the natural substance amounts to $35^{\circ} 14'$. This alcohol appears, therefore, to be very strongly subject to racemisation, even in nature. By the facts stated it has, therefore, been proved that linaloöl consists of a simple optically active terpene alcohol; the incorrectness of BARBIER's formula for linaloöl and myrcenol has been demonstrated, whilst the linaloöl formula of TIEMANN and SEMMLER has received support.

Physics. — “*On the propagation of light in a biaxial crystal around a centre of vibration.*” By H. B. A. BOCKWINKEL. (Communicated by Prof. H. A. LORENTZ).

(Communicated in the Meeting of January 1906).

In the electromagnetic theory of light, it is of interest to determine the electromagnetic field in a crystal due to an action, taking place in a certain centre O . In order to fix the ideas, we shall assume, that in an element of space τ at the point O there are certain periodic electromotive forces ($E. M. F.$). There will then be a radiation of energy from O in every direction, the amount of which will depend on this direction with respect to that of the $E. M. F.$ and to those of the axes of electric symmetry. Our object is to investigate this dependence, at least for points at a great distance from O . We might for this purpose use the results of GRÜNWALD¹⁾; this physicist however takes the equations in the form they assume for a rigid elastic body and does not operate with an $E. M. F.$ as mentioned above; we shall therefore treat the problem independently. Our method will consist in reducing the question to one of plane waves, by using a formula, proved by Prof. LORENTZ. In this formula a continuous function of the coordinates is represented by an integral over the solid angles of all cones having their vertices in O and filling the whole space. If the $E. M. F.$ is \mathfrak{E} then

$$\mathfrak{E} = - \int \frac{1}{8\pi^2} \frac{\partial^2 \mathfrak{B}}{\partial n^2} d\omega, \dots \dots \dots (1)$$

where dn is the element of a line of arbitrary direction within the cone $d\omega$ and \mathfrak{B} a vector given by

$$\mathfrak{B} = \int \mathfrak{E} d\sigma, \dots \dots \dots (2)$$

the integral being taken over the plane, passing through the point considered, perpendicularly to n . Hence, \mathfrak{B} depends on the coordinates, but in such a way as to be constant in every plane perpendicular to n . By (1) the original $E. M. F.$ has now been decomposed into a great number of infinitely small vectors, the effect of which can easily be calculated, each of them being constant in planes of a certain direction. Thus we determine the field, produced by each of the elements of the integral (1) and then compose all the fields obtained in this way into one resulting field, which,

¹⁾ J. GRÜNWALD. Über die Ausbreitung der Wellenbewegungen in optisch zweiaxigen elastischen Medien, BOLTZMANN Festschrift (1904), p. 518.

according to the principle of superposition, will really be the one produced by the whole E. M. F. Each of the separate very small fields will consist in a propagation of plane waves having the same direction as the planes in which the corresponding element of the E. M. F. is constant. The problem will therefore indeed be reduced to one of plane waves.

§ 2. In order to find the small field, corresponding to a cone of definite direction, we shall take a system of coordinates OX', OY', OZ' , the axis OZ' coinciding with the axis of the chosen cone and OX', OY' respectively with the two directions of the dielectric displacement, belonging to plane waves, normal to OZ' . The wave that has its dielectric displacement along OX' will be called "the first wave"; the other "the second wave".

Again we take a system of coordinates OX, OY, OZ , the axes of which coincide with the axes of electric symmetry. Denoting the components of the electric force along the first axes by $\mathfrak{E}_x, \mathfrak{E}_y, \mathfrak{E}_z$

and supposing all quantities to contain the factor $e^{i\frac{2\pi}{T}t}$ we have to satisfy the following equations

$$\left. \begin{aligned} \Delta \mathfrak{E}_x - \frac{\partial}{\partial x'} (\text{div. } \mathfrak{E}) &= -\frac{4\pi^2}{T^2 c^2} \left[\epsilon_{11} (\mathfrak{E}_x + \mathfrak{E}_x^e) + \epsilon_{12} (\mathfrak{E}_y + \mathfrak{E}_y^e) + \epsilon_{13} (\mathfrak{E}_z + \mathfrak{E}_z^e) \right] \\ \Delta \mathfrak{E}_y - \frac{\partial}{\partial y'} (\text{div. } \mathfrak{E}) &= -\frac{4\pi^2}{T^2 c^2} \left[\epsilon_{12} (\mathfrak{E}_x + \mathfrak{E}_x^e) + \epsilon_{22} (\mathfrak{E}_y + \mathfrak{E}_y^e) + \epsilon_{23} (\mathfrak{E}_z + \mathfrak{E}_z^e) \right] \\ \Delta \mathfrak{E}_z - \frac{\partial}{\partial z'} (\text{div. } \mathfrak{E}) &= -\frac{4\pi^2}{T^2 c^2} \left[\epsilon_{13} (\mathfrak{E}_x + \mathfrak{E}_x^e) + \epsilon_{23} (\mathfrak{E}_y + \mathfrak{E}_y^e) + \epsilon_{33} (\mathfrak{E}_z + \mathfrak{E}_z^e) \right] \end{aligned} \right\} \quad (3)$$

It will not give rise to any misunderstanding that we have denoted here by \mathfrak{E}^e the expression $-\frac{d\omega}{8\pi^2} \frac{\partial^2 \mathfrak{B}}{\partial z'^2}$.

The quantities ϵ , occurring in these formulae, have particular properties, because they relate to *special* directions. These properties will show themselves in the following development. Since, according to the preceding considerations, \mathfrak{E}^e depends only upon z' , we shall find for \mathfrak{E} a solution, likewise containing only z' . By this hypothesis the equations (3) become

$$\left. \begin{aligned} \frac{\partial^2 \mathfrak{E}_x}{\partial z'^2} &= -\frac{4\pi^2}{c^2 T^2} \left[\epsilon_{11} (\mathfrak{E}_x + \mathfrak{E}_x^e) + \epsilon_{12} (\mathfrak{E}_y + \mathfrak{E}_y^e) + \epsilon_{13} (\mathfrak{E}_z + \mathfrak{E}_z^e) \right] \\ \frac{\partial^2 \mathfrak{E}_y}{\partial z'^2} &= -\frac{4\pi^2}{c^2 T^2} \left[\epsilon_{12} (\mathfrak{E}_x + \mathfrak{E}_x^e) + \epsilon_{22} (\mathfrak{E}_y + \mathfrak{E}_y^e) + \epsilon_{23} (\mathfrak{E}_z + \mathfrak{E}_z^e) \right] \\ 0 &= \epsilon_{13} (\mathfrak{E}_x + \mathfrak{E}_x^e) + \epsilon_{23} (\mathfrak{E}_y + \mathfrak{E}_y^e) + \epsilon_{33} (\mathfrak{E}_z + \mathfrak{E}_z^e) \end{aligned} \right\} \quad (4)$$

§ 3. The last equation of (4) shows, that there is no dielectric displacement in the z' -direction. Further it is evident from these equations, that \mathfrak{E}_x^e has no share in the disturbance of the state of the aether at a distant point. Indeed, \mathfrak{E}_x^e and \mathfrak{E}_y^e being zero, the equations are satisfied by the solution

$$\mathfrak{E}_x = 0, \quad \mathfrak{E}_y = 0, \quad \mathfrak{E}_z = -\mathfrak{E}_z^e.$$

At the distant point \mathfrak{E}_z^e is zero, therefore \mathfrak{E}_z is so likewise. Electromotive forces acting within a layer bounded by two parallel planes and directed perpendicularly to these planes, do not therefore produce any disturbance of equilibrium at a distant point.

We eliminate \mathfrak{E}_z between the first and the third and between the second and the third equation.

This gives

$$\begin{aligned} \frac{\partial^2 \mathfrak{E}_x}{\partial z'^2} &= -\frac{4\pi^2}{c^2 T^2} \left[\left(\epsilon_{11} - \frac{\epsilon_{13}^2}{\epsilon_{33}} \right) (\mathfrak{E}_x + \mathfrak{E}_x^e) + \left(\epsilon_{12} - \frac{\epsilon_{13}\epsilon_{23}}{\epsilon_{33}} \right) (\mathfrak{E}_y + \mathfrak{E}_y^e) \right] \\ \frac{\partial^2 \mathfrak{E}_y}{\partial z'^2} &= -\frac{4\pi^2}{c^2 T^2} \left[\left(\epsilon_{12} - \frac{\epsilon_{13}\epsilon_{23}}{\epsilon_{33}} \right) (\mathfrak{E}_x + \mathfrak{E}_x^e) + \left(\epsilon_{22} - \frac{\epsilon_{23}^2}{\epsilon_{33}} \right) (\mathfrak{E}_y + \mathfrak{E}_y^e) \right]. \end{aligned}$$

According to what has already been said, these equations, if no E. M. F. are acting, must have one solution in which \mathfrak{E}_x is zero, and another in which \mathfrak{E}_y vanishes. This would follow from the equations themselves, if we knew the above mentioned properties of the quantities ϵ , occurring in them. Conversely, we shall be able to deduce these properties from the knowledge that the two solutions must satisfy the equations. Indeed these solutions can only hold if

$$\epsilon_{12} - \frac{\epsilon_{13}\epsilon_{23}}{\epsilon_{33}} = 0$$

and

$$V_x^2 = \frac{c^2}{\epsilon_{11} - \frac{\epsilon_{13}^2}{\epsilon_{33}}}, \quad V_y^2 = \frac{c^2}{\epsilon_{22} - \frac{\epsilon_{23}^2}{\epsilon_{33}}}$$

where V_x and V_y are the velocities of the plane waves in the two cases. By this the equations take the form

$$\frac{\partial^2 \mathfrak{E}_x}{\partial z'^2} = -\frac{4\pi^2}{T^2 V_x^2} (\mathfrak{E}_x + \mathfrak{E}_x^e), \quad \frac{\partial^2 \mathfrak{E}_y}{\partial z'^2} = -\frac{4\pi^2}{T^2 V_y^2} (\mathfrak{E}_y + \mathfrak{E}_y^e) \quad (5)$$

whereas the third equation of (4) gives \mathfrak{E}_z when \mathfrak{E}_x and \mathfrak{E}_y are known. We see from (5) that \mathfrak{E}_x depends only on \mathfrak{E}_x^e , and \mathfrak{E}_y only on \mathfrak{E}_y^e , further that both equations have the same form. We can

therefore confine ourselves to considering only the first; in doing so we shall write V instead of V_x . We shall have to remember however that after having found the result that is due to the X' -components of the E. M. F. we have still to add to this a second amount given by the Y' -component; this amount can be written down at once by analogy with the first.

§ 4. The general solution of the equation

$$\frac{\partial^2 \mathfrak{E}_x}{\partial z'^2} = -\frac{4\pi^2}{T^2 V^2} (\mathfrak{E}_x + \mathfrak{E}_x^c)$$

is given by

$$\mathfrak{E}_x = \frac{i\pi}{TV} e^{i\frac{2\pi z'}{TV}} \int_{g_2}^{z'} \mathfrak{E}_x^c e^{-i\frac{2\pi z'}{TV}} dz' - \frac{i\pi}{TV} e^{-i\frac{2\pi z'}{TV}} \int_{g_1}^{z'} \mathfrak{E}_x^c e^{i\frac{2\pi z'}{TV}} dz'. \quad (6)$$

The lower limit of these integrals is arbitrary, so that, as could be expected, two arbitrary constants occur in the solution. It is easily understood, that in the final result there will likewise be a certain indefiniteness. Indeed both a propagation towards O and one from O will be contained in it. It is sufficient for our present purpose to consider only the first solution and in order to leave aside the second we have to give completely definite values to the constants, as will appear in the following manner. We consider the two planes perpendicular to OZ' , tangent to the boundary surface of the space τ ; let these planes be determined by the equations

$$z' = -h_1 \quad \text{and} \quad z' = h_2.$$

Then, since \mathfrak{E}_x^c stands for

$$-\frac{1}{8\pi^2} \frac{\partial^2 \mathfrak{B}}{\partial z'^2} dw,$$

it will differ from zero between the planes and will be zero in the space outside them. The first integral of (6) must vanish for

$$z' > h_2$$

and the second for

$$z' < -h_1.$$

This is only possible, if

$$g_1 \leq -h_1 \quad \text{and} \\ g_2 \geq h_2.$$

For the rest g_1 and g_2 may have any value satisfying these inequalities; it is evident that the result of the integrations will always be the same, if we take into account what has been said about the

values of \mathfrak{E}_x . We shall therefore put $g_1 = -h_1$ and $g_2 = h_2$, so that

$$\mathfrak{E}_x = \frac{i d\omega}{8\pi TV} e^{-i \frac{2\pi z'}{TV}} \int_{-h_1}^{z'} \frac{\partial^2 \mathfrak{B}_x}{\partial z'^2} e^{i \frac{2\pi z'}{TV}} dz' - \frac{i d\omega}{8\pi TV} e^{i \frac{2\pi z'}{TV}} \int_{h_2}^{z'} \frac{\partial^2 \mathfrak{B}_x}{\partial z'^2} e^{-i \frac{2\pi z'}{TV}} dz' \quad (7)$$

§ 5. In effecting these integrations we have to distinguish whether or no the point P , for which we intend to determine the state of radiation, lies between the two just mentioned tangent planes. First taking the latter case, the second integral of (7) is zero for positive values of z' , whereas in the first case we may take h_2 instead of z' for the upper limit. Integration by parts gives

$$\int_{-h_1}^{h_2} \frac{\partial^2 \mathfrak{B}_x}{\partial z'^2} e^{i \frac{2\pi z'}{TV}} dz' = \left[\frac{\partial \mathfrak{B}_x}{\partial z'} e^{i \frac{2\pi z'}{TV}} \right]_{-h_1}^{h_2} - i \frac{2\pi}{TV} \int_{-h_1}^{h_2} \mathfrak{B}_x e^{i \frac{2\pi z'}{TV}} dz'.$$

Now \mathfrak{E}_x can only be represented by (1) if it is a *continuous* function of the co-ordinates, but we may imagine nevertheless that at the boundary of the space τ , \mathfrak{B} and $\partial \mathfrak{B} / \partial z'$ have arbitrarily small values. These quantities may therefore be taken zero at the boundary; as to \mathfrak{B} , this has already been done in the considerations of the preceding paragraph. Hence the first term, given by the integration by parts, vanishes; the second may again be integrated by parts, so that finally

$$\int_{-h_1}^{h_2} \frac{\partial^2 \mathfrak{B}_x}{\partial z'^2} e^{i \frac{2\pi z'}{TV}} dz' = - \frac{4\pi^2}{T^2 V^2} \int_{-h_1}^{h_2} \mathfrak{B}_x e^{i \frac{2\pi z'}{TV}} dz'.$$

The exponential factor under the sign of integration may be replaced by 1. Indeed, if a certain length l , of the same order of magnitude as the linear dimensions of the space τ is very small in comparison with the wavelength λ of light, we may omit terms containing products of $\frac{\tau}{\lambda^2}$ and quantities of the order $\frac{l}{2}$. Now

$$\mathfrak{B}_x = \int \mathfrak{E}_x d\sigma$$

the integral taken over the portion of a plane $z' = \text{const.}$ lying within τ . From this we infer

$$\int_{-h_1}^{h_2} \mathfrak{B}_x dz' = \int \mathfrak{E}_x d\tau$$

integrated over the volume τ . We shall represent this integral by

$\mathfrak{E}_x^e \tau$, denoting by \mathfrak{E}_x^e a certain mean value of the X' -component of the E. M. F. within τ . We may now write

$$\int_{-h_1}^{h_2} \frac{\partial^2 \mathfrak{B}_x}{\partial z'^2} e^{i \frac{2\pi z'}{TV}} dz' = - \frac{4\pi^2 \mathfrak{E}_x^e \tau}{T^2 V^2}$$

Similarly

$$\int_{-h_1}^{h_2} \frac{\partial^2 \mathfrak{B}_x}{\partial z'^2} e^{-i \frac{2\pi z'}{TV}} dz' = - \frac{4\pi^2 \mathfrak{E}_x^e \tau}{T^2 V^2},$$

an integral that has to be used for negative values of z' less than $-h_1$.

§ 6. If lastly

$$-h_1 < z' < h_2$$

the point P lies between the tangent planes and *both* integrals differ from zero. We find by some transformations

$$\begin{aligned} \int_{-h_1}^{z'} \frac{\partial^2 \mathfrak{B}_x}{\partial z'^2} e^{i \frac{2\pi z'}{TV}} dz' &= \frac{\partial \mathfrak{B}_x}{\partial z'} e^{i \frac{2\pi z'}{TV}} - i \frac{2\pi}{TV} \mathfrak{B}_x e^{i \frac{2\pi z'}{TV}} - \frac{4\pi^2}{T^2 V^2} \int_{-h_1}^{z'} \mathfrak{B}_x e^{i \frac{2\pi z'}{TV}} dz' \\ \int_{h_2}^{z'} \frac{\partial^2 \mathfrak{B}_x}{\partial z'^2} e^{-i \frac{2\pi z'}{TV}} dz' &= \frac{\partial \mathfrak{B}_x}{\partial z'} e^{-i \frac{2\pi z'}{TV}} + i \frac{2\pi}{TV} \mathfrak{B}_x e^{-i \frac{2\pi z'}{TV}} - \\ &\quad - \frac{4\pi^2}{T^2 V^2} \int_{h_2}^{z'} \mathfrak{B}_x e^{-i \frac{2\pi z'}{TV}} dz'. \end{aligned}$$

So that in this case the X' -component of the electric force is given by

$$\begin{aligned} \mathfrak{E}_x = \frac{i d\omega}{8\pi T V} \left[-i \frac{4\pi}{TV} \mathfrak{B}_x - \frac{4\pi^2}{T^2 V^2} e^{-i \frac{2\pi z'}{TV}} \int_{-h_1}^{z'} \mathfrak{B}_x e^{i \frac{2\pi z'}{TV}} dz' - \right. \\ \left. - \frac{4\pi^2}{T^2 V^2} e^{i \frac{2\pi z'}{TV}} \int_{h_2}^{z'} \mathfrak{B}_x e^{-i \frac{2\pi z'}{TV}} dz' \right]. \end{aligned}$$

Since z' lies between $-h_1$ and h_2 , we may replace the exponential factors by 1, both before and behind the sign of integration. Then we find finally

1st. If P lies between the tangent planes

$$\mathfrak{E}_x = \frac{\mathfrak{B}_x}{2T^2 V^2} d\omega - \frac{i\pi \mathfrak{E}_x^e \tau}{2T^2 V^2} d\omega$$

2nd. If P lies outside these planes

a. For positive values of z'

$$\mathcal{E}_{x'} = -\frac{i\pi\mathcal{E}_x^e\tau}{2T^3V^3}e^{-i\frac{2\pi z'}{TV}}d\omega$$

b. For negative values of z'

$$\mathcal{E}_{x'} = -\frac{i\pi\mathcal{E}_x^e\tau}{2T^3V^3}e^{i\frac{2\pi z'}{TV}}d\omega$$

The Z' -component of the electric force consists of two parts, one of which corresponds to $\mathcal{E}_{x'}$, the other to $\mathcal{E}_{y'}$. Having already omitted the Y' -component, we shall take only the first part, $\mathcal{E}_{x'1}$, of the Z' -component and add the second part $\mathcal{E}_{x'2}$ to the Y' -component afterwards. Then by the third equation of (4)

$$\mathcal{E}_{x'1} - \frac{1}{8\pi^2} \frac{\partial^2 \mathcal{E}_{x'}}{\partial z'^2} d\omega = -\frac{\epsilon_{13}}{\epsilon_{33}} \left\{ \mathcal{E}_{x'} - \frac{1}{8\pi^2} \frac{\partial^2 \mathcal{E}_{x'}}{\partial z'^2} d\omega \right\}.$$

It appears from this that outside the tangent planes $\mathcal{E}_{x'}$ and $\mathcal{E}_{x'}$ are connected with each other in the way they always are in the case of plane waves. We may therefore represent the electric force by $\frac{\mathcal{E}_{x'}}{\cos \vartheta}$ if ϑ is the angle between this vector and the corresponding dielectric displacement in a system of plane waves. Finally we have the following equations for the components of the electric force along the axes of symmetry

$$\left. \begin{aligned} \mathcal{E}_x &= -\frac{i\pi\alpha\mathcal{E}_x^e\tau}{2T^3V^3\cos\vartheta}e^{-i\frac{2\pi z'}{TV}}d\omega, \\ \mathcal{E}_y &= -\frac{i\pi\beta\mathcal{E}_x^e\tau}{2T^3V^3\cos\vartheta}e^{-i\frac{2\pi z'}{TV}}d\omega, \\ \mathcal{E}_z &= -\frac{i\pi\gamma\mathcal{E}_x^e\tau}{2T^3V^3\cos\vartheta}e^{-i\frac{2\pi z'}{TV}}d\omega, \end{aligned} \right\} \dots \dots \dots (8)$$

where α , β and γ are the direction cosines of the electric force with respect to the axes of symmetry. For negative values of z' the same formulae will apply, provided that z' be replaced by $-z'$.

§ 7. In the preceding equations the symbols \mathcal{E}_x , \mathcal{E}_y and \mathcal{E}_z were used for the (small) electric force, produced by a single element of the integral (1) in a point P , lying at a given distance r from the origin O . We have seen that the expression for this small electric force took a different form according to the point P lying or not

lying between the before mentioned tangent planes. Now the directions for which P lies *inside* these planes are those *excluded* by a certain cone K , which may be defined as the locus of all normals to another cone, having its vertex in P and tangent to the boundary of the element of space τ . On the other hand, all directions of wave normals, for which P lies *outside* the tangent planes are *included* by the cone K . It is clear that this cone will differ infinitely little from the plane passing through O perpendicularly to OP .

We may therefore find the total electric force by integrating the right hand members of the equations (8) with respect to all directions lying within K and then adding to the result the quantity obtained by integrating the expressions relating to the remaining directions. In effecting the first integration we must replace z' by $-z'$ for negative values of z' , according to the remark made at the end of § 6. But we may as well limit the integration to half the cone K multiplying the result by 2. Again, we may extend this integration to the plane F ; indeed the right hand members of (8) contain τ as a factor, so that it does not matter, whether or no an infinitely small solid angle is included in this integration.

It remains to consider the expressions

$$\mathcal{E}_x = \frac{\mathfrak{M}_x}{2T^3V^3} d\omega - \frac{i\pi \mathcal{E}_x \tau}{2T^3V^3} d\omega,$$

$$\mathcal{E}_{x'} = \frac{1}{8\pi^2} \left(\frac{\partial^2 \mathfrak{M}_x}{\partial z'^2} d\omega + \frac{\epsilon_{12}}{\epsilon_{22}} \frac{\partial^2 \mathfrak{M}_x}{\partial z'^2} d\omega \right) - \frac{\epsilon_{12}}{\epsilon_{22}} \mathcal{E}_x,$$

which have to be integrated over all directions outside the cone K .

Now, from these expressions we get the components along the axes of symmetry by multiplying them by finite factors. It is easily seen that terms already containing the factor τ may therefore be omitted, so that we may write

$$\mathcal{E}_x = \frac{\mathfrak{M}_x}{2T^3V^3} d\omega,$$

$$\mathcal{E}_{x'} = -\frac{\epsilon_{12}}{\epsilon_{22}} \mathcal{E}_x + \frac{1}{8\pi^2} \left(\frac{\partial^2 \mathfrak{M}_x}{\partial z'^2} + \frac{\epsilon_{12}}{\epsilon_{22}} \frac{\partial^2 \mathfrak{M}_x}{\partial z'^2} \right) d\omega.$$

§ 8. We shall resolve this last vector into two other vectors, the components of the first being

$$\mathcal{E}_x = \frac{\mathfrak{M}_x}{2T^3V^3}, \quad \mathcal{E}_{x'} = -\frac{\epsilon_{12}}{\epsilon_{22}} \mathcal{E}_x,$$

and those of the second

$$\mathcal{E}_x = 0, \quad \mathcal{E}_{x'} = \frac{1}{8\pi^2} \left(\frac{\partial^2 \mathfrak{M}_x}{\partial z'^2} + \frac{\epsilon_{12}}{\epsilon_{22}} \frac{\partial^2 \mathfrak{M}_x}{\partial z'^2} \right) d\omega.$$

The first vector has again the same direction as the electric force in plane waves whose normal coincides with the direction we are considering; its components along the axes of symmetry are therefore

$$\mathfrak{E}_x = \frac{\alpha \mathfrak{M}_x}{2 T^2 V^2 \cos \vartheta} d\omega, \quad \mathfrak{E}_y = \frac{\beta \mathfrak{M}_x}{2 T^2 V^2 \cos \vartheta} d\omega, \quad \mathfrak{E}_z = \frac{\gamma \mathfrak{M}_x}{2 T^2 V^2 \cos \vartheta} d\omega.$$

Now \mathfrak{M}_x , is of the order l^3 and the integration is to be effected over a solid angle of the order l . Thus, confining ourselves to directions in a single plane passing through OP , we may regard as constants the quantities α, V and $\cos \vartheta$, assigning to them the values they take in the plane F .

We determine an arbitrary direction in the plane passing through OP by the angle ξ which it makes with OP and its azimuth χ with respect to a fixed plane also passing through OP . Then

$$d\omega = \sin \xi \, d\xi \, d\chi.$$

Now we have for the direction considered

$$W_x = \int \mathfrak{E}_x \, d\sigma$$

the integral being extended to the portion inside τ of a plane G , passing through P perpendicularly to that direction. If q is the normal drawn from O towards G , we have

$$q = r \cos \xi, \\ |dq| = r \sin \xi \, d\xi,$$

giving

$$d\omega = \frac{1}{r} |dq| \, d\chi,$$

and

$$\mathfrak{E}_x = \frac{1}{2rT^2} \int_0^{2\pi} \frac{\alpha}{V^2 \cos \vartheta} d\chi \int \mathfrak{M}_x |dq|.$$

Here for each particular value of χ , the latter integral is to be extended to all values that can be given to ξ or q . Further

$$\int \mathfrak{M}_x |dq| = \int |dq| \int \mathfrak{E}_x \, d\sigma = \iint \mathfrak{E}_x \, d\sigma |dq|,$$

whereas

$$d\sigma |dq|$$

is the element of volume of an infinitely small cylinder whose upper and lower base are formed respectively by one of the surface elements of G and of an infinitely near plane G' , the generating lines of the cylinder being perpendicular to G . It follows from this that

$$\iint \mathfrak{E}_x^e d\sigma |dq|$$

is the volume-integral of \mathfrak{E}_x^e , taken over the whole volume of τ .

We have already written for this integral $\mathfrak{E}_x^e \tau$, denoting by \mathfrak{E}_x^e a certain mean value (§ 5). Hence, the *first* part of the components of the electric force resulting from the integration with respect to the directions outside the cone K , becomes

$$\begin{aligned} \mathfrak{E}_x &= \frac{1}{2T^2 r} \int_0^{2\pi} \frac{\alpha \mathfrak{E}_x \tau}{V^2 \cos \vartheta} d\chi, \quad \mathfrak{E}_y = \frac{1}{2T^2 r} \int_0^{2\pi} \frac{\beta \mathfrak{E}_x \tau}{V^2 \cos \vartheta} d\chi, \quad \mathfrak{E}_z = \\ &= \frac{1}{2T^2 r} \int_0^{2\pi} \frac{\gamma \mathfrak{E}_x \tau}{V^2 \cos \vartheta} d\chi \dots \dots \dots (9) \end{aligned}$$

The second part results from a similar integration of the second vector

$$\mathfrak{E}_x = 0, \quad \mathfrak{E}_{x1} = \frac{1}{8\pi^2} \left(\frac{\partial^2 \mathfrak{B}_{x'}}{\partial z'^2} + \frac{\varepsilon_{11}}{\varepsilon_{11}} \frac{\partial^2 \mathfrak{B}_{x'}}{\partial z'^2} \right) d\omega.$$

Now it will appear further on, that we can only determine the exact value of those terms, in which the denominator contains the first power of r . We may therefore confine ourselves to such terms in the whole course of our calculations. The cone over which we have to integrate being of the order l/r , we may omit terms, which already contain r in the denominator. It will be evident therefore that instead of

$$\frac{\partial^2 \mathfrak{B}_{x'}}{\partial z'^2} \text{ and } \frac{\partial^2 \mathfrak{B}_{x'}}{\partial z'^2}$$

we may take the values of these quantities, corresponding to that wave-normal, in the meridian plane passing through OP , which lies at the same time in the plane F . If dz' is a line-element of that wave-normal, we have to consider the integrals

$$\int \frac{\partial^2 \mathfrak{B}_{x'}}{\partial z'^2} dz' \text{ and } \int \frac{\partial^2 \mathfrak{B}_{x'}}{\partial z'^2} dz'$$

which evidently are zero, $\frac{\partial \mathfrak{B}}{\partial z'}$ being zero at the boundary of τ . It appears in this way that we need not at all consider the second vector.

§ 9. We now proceed to effect the integration of the right hand members of the equations (8) so far as is necessary in order to obtain the terms with $\frac{1}{r}$. We shall take the real parts of all expres-

sions and represent henceforth by \mathfrak{E} the whole electric force. Then, if $\mathfrak{E} = b \cos 2\pi \frac{t}{T}$, we shall have

$$\mathfrak{E}_x = \int \frac{\pi a b x' \tau}{T^3 V^3 \cos \vartheta} \sin \frac{2\pi}{T} \left(t - \frac{z'}{V} \right) d\omega, \quad \dots \quad (10)$$

integrated over all directions on that side of F where z' has positive values. We therefore obtain the resultant luminous vibration in an arbitrary point P as the sum of small vibrations, belonging to a great number of systems of plane waves of all possible directions. These vibrations differ from each other in amplitude and in phase. The changes of phase are determined by those of the quantity

$$\frac{z'}{TV}$$

Since TV means the wave-length in the crystal for the direction considered and $z' = r \cos \xi$, the phase will vary very much by small variations of ξ , i.e., of the direction of the wave system in question. There is one direction for which

$$\frac{z'}{TV}$$

takes a maximum value. This is the direction of the wave-normal OQ to which OP corresponds as first ray. Indeed, z'/TV is proportional to the time in which the vibrations of a certain wave-system arrive at P and this time is really a maximum for the system whose normal is OQ . We shall prove, that the resultant vibration at P is the same as it would be, if we had only to do with wave systems of this latter direction and of directions in the immediate vicinity of it. To this effect we shall fix our attention on an arbitrary normal ON , making an angle ϕ with OQ , writing ψ for the azimuth of the plane NOQ with respect to a fixed plane, which passes through OQ , and for which we might take the plane POQ . We shall not however introduce ψ and ϕ as variables but u and

$$u = \frac{V_0}{V} \cos \xi,$$

if V_0 is the velocity of propagation of the plane wave, having OQ for its normal. Further we put

$$\frac{2\pi t}{T} = h, \quad \frac{2\pi r}{TV_0} = g, \quad d\omega = \sin \phi \frac{\partial \phi}{\partial u} du d\psi.$$

Then

$$\mathfrak{E}_x = - \int_0^{2\pi} \int_{u_0}^0 \frac{\pi a b x' \tau}{T^3 V^3 \cos \vartheta} \sin (gu - h) \sin \phi \frac{\partial \phi}{\partial u} du d\psi, \quad \dots \quad (11)$$

if u_0 is the value of u for the direction OQ . Indeed the directions for which $u = \text{const.}$ lie on a cone surrounding the line OQ , just because u is a maximum for that line. We first integrate with respect to ψ and put

$$-\int_0^{2\pi} \frac{\pi a b_x \tau}{T^3 V^3 \cos \vartheta} \sin \phi \frac{\partial \phi}{\partial u} d\psi = f(u) (12)$$

The result is

$$\mathfrak{E}_x = \int_{u_0}^0 f(u) \sin(gu - h) du (13)$$

§ 10. An integral such as (13) has already been considered by KIRCHHOFF. For great values of g it approaches uniformly to zero and at infinity it may be represented by a development of the form

$$\frac{a_1}{g} + \frac{a_2}{g^2} +$$

It is only the coefficient a_1 that can be found. Integration by parts of the integral gives

$$\int_{u_0}^0 f(u) \sin(gu - h) du = \frac{f(u_0) \cos(gu_0 - h) - f(0) \cos h}{g} + \frac{a_1}{g^2} + . . . (14)$$

The first term, taken by itself, gives a sufficiently exact result for points P , lying at distances r from O , which are large in comparison with the wavelength of light; in the following development we have in view only such points as satisfy this condition. We put therefore

$$\int_{u_0}^0 f(u) \sin(gu - h) du = \frac{f(u_0) \cos(gu_0 - h) - f(0) \cos h}{g} . . . (14a)$$

We shall first consider the part

$$-\frac{f(0) \cos h}{g} = \frac{TV_0}{2\pi r} \cos 2\pi \frac{t}{T} \int_0^{2\pi} \left[\frac{\pi a b_x \tau}{T^3 V^3 \cos \vartheta} \sin \phi \frac{\partial \phi}{\partial u} \right]_{u=0} d\psi .$$

Now

$$\sin \phi \frac{\partial \phi}{\partial u} = -\frac{\partial(\cos \phi)}{\partial(\cos \xi)} \cdot \frac{\partial(\cos \xi)}{\partial u} ,$$

$$\frac{\partial u}{\partial(\cos \xi)} = \frac{\partial}{\partial(\cos \xi)} \left[\frac{V_0}{V} \cos \xi \right] = \frac{V_0}{V} + \cos \xi \frac{\partial}{\partial(\cos \xi)} \left[\frac{V_0}{V} \right] ,$$

so that for $u = 0$ or $\cos \xi = 0$

$$\left[\sin \phi \frac{\partial \phi}{\partial u} \right]_{u=0} = - \frac{V}{V_0} \left[\frac{\partial(\cos \phi)}{\partial(\cos \xi)} \right]_{u=0}.$$

We may further deduce from the consideration of the spherical triangle, defined by the directions ON , OQ and OP , that for $u=0$

$$\frac{\partial(\cos \phi)}{\partial(\cos \xi)} = \left(\frac{d\chi}{d\psi} \right)_{u=0},$$

so that

$$\left(\sin \phi \frac{\partial \phi}{\partial u} \right)_{u=0} = - \frac{V}{V_0} \left(\frac{d\chi}{d\psi} \right)_{u=0}$$

and

$$-\frac{f(0)\cosh}{g} = -\frac{1}{2T^2 r} \cos \frac{2\pi t}{T} \int_0^{2\pi} \frac{\alpha b_x \tau}{V^2 \cos \vartheta} d\chi.$$

The real part of the expression (9), added to this result gives exactly zero, so that, as we could have expected, there remains in \mathfrak{E}_x no term with only $\cos 2\pi t/T$. We need hardly add that this is equally the case with \mathfrak{E}_y and \mathfrak{E}_z .

Finally we have to determine $f(u_0)$. Let us denote by Ω the solid angle of a cone, formed by directions for which u is constant, then

$$d\Omega = du \int_0^{2\pi} \sin \phi \frac{\partial \phi}{\partial u} d\psi. \quad \dots \quad (15)$$

Now by (12) we have

$$f(u_0) = - \frac{\pi \alpha_0 b_{x_0} \tau}{T^2 V_0^2 \cos \vartheta_0} \int_0^{2\pi} \left(\sin \phi \frac{\partial \phi}{\partial u} \right)_{u=u_0} d\psi,$$

and with a view to (15) we may write for this

$$f(u_0) = - \frac{\pi \alpha_0 b_{x_0} \tau}{T^2 V_0^2 \cos \vartheta_0} \left(\frac{d\Omega}{du} \right)_{u=u_0}.$$

The solid angle $d\Omega_0$ of an infinitely small cone with axis OQ may be found in the following manner. We imagine the wave-surface W , passing through P , and the polar surface R of W with respect to a sphere of radius unity. Then the point corresponding to P will be the point of intersection Q of OQ and R . Further we take a point P' on OP prolonged, close to P and describe from P' the cone tangent to W . The normals drawn from O to this cone will lie on a second cone and this is the locus of all directions for which u has the constant value

$$\frac{OP}{OP'} \cos \vartheta_0$$

The infinitely small cone of normals will intersect R in a curve lying in a plane, normal to OP ; the plane touching R at the point Q is also normal to OP . Let these last two planes, which are therefore parallel, cut OP in S' and S . Then

$$OS \times OP = 1 \quad OS' \times OP' = 1,$$

and

$$u = OS' \cdot OP \cos \vartheta_0, \\ du_0 = -SS' \cdot OP \cos \vartheta_0.$$

Further

$$d\Omega_0 = \frac{\cos \vartheta_0}{OQ^2} d\sigma,$$

if $d\sigma$ is the infinitely small surface of the just mentioned plane curve. But we have also

$$d\sigma = 2\pi \sqrt{\varrho_0 \varrho'_0} SS'$$

if ϱ_0 and ϱ'_0 are the two principal radii of curvature of R at the point Q . Combining the obtained equations we find therefore

$$\left(\frac{d\Omega}{du} \right)_{u=u_0} = - \frac{2\pi \sqrt{\varrho_0 \varrho'_0}}{OQ^2 OP},$$

or since $OP = r$ and $\frac{1}{OQ} = OP \cos \vartheta_0 = r \cos \vartheta_0$,

$$\left(\frac{d\Omega}{du} \right)_{u=u_0} = -2\pi r \sqrt{\varrho_0 \varrho'_0} \cos^2 \vartheta_0,$$

so that

$$f(u_0) \frac{\cos(gu_0 - h)}{g} = - \frac{\pi \alpha_0 \mathfrak{b}_{x_0} \tau}{T^2 V_0^2 \cos \vartheta_0} - 2\pi r \sqrt{\varrho_0 \varrho'_0} \cos^2 \vartheta_0 \cdot \frac{TV_0}{2\pi r} \cos(gu_0 - h)$$

or by (13) and (14)

$$\mathfrak{E}_x = f(u_0) \frac{\cos(gu_0 - h)}{g} = \frac{\pi \alpha_0 \mathfrak{b}_{x_0} \tau \sqrt{\varrho_0 \varrho'_0} \cos \vartheta_0}{T^2 V_0^2} \cos \frac{2\pi}{T} \left(t - \frac{r}{p_0} \right),$$

if p_0 is the velocity of propagation of the ray OP , as it is defined for plane waves. Thus the electric force appears to have the same direction as it has for plane waves whose corresponding rays coincide with OP . Its magnitude is given by

$$\mathfrak{E} = \frac{\pi \mathfrak{b}_{x_0} \tau \sqrt{\varrho_0 \varrho'_0} \cos \vartheta_0}{T^2 V_0^2} \cos \frac{2\pi}{T} \left(t - \frac{r}{p_0} \right).$$

§ 11. We must add to this a second vibration which may be obtained by the composition of all wave systems due to the Y' -components of the infinitely small vectors into which the original E. M. F. has been divided. It is this action we have left aside in

§ 3; the total electric force produced by it is given by

$$\mathcal{E} = \frac{\pi b_{y1}' \tau \sqrt{Q_1 Q_1'} \cos \vartheta_1}{T^2 V_1'} \cos \frac{2\pi}{T} \left(t - \frac{r}{p_1} \right),$$

if we distinguish by the index 1 the quantities corresponding to the *second* plane wave for which *OP* is the direction of the ray. The magnetic force too has in both cases the ordinary direction and may be derived from the electric force by multiplying respectively by

$$\frac{c}{p_0} = \frac{c \cos \vartheta_0}{V_0} \quad \text{and} \quad \frac{c}{p_1} = \frac{c \cos \vartheta_1}{V_1},$$

so that the flow of energy is given by

$$\mathcal{E} = \frac{c \cos \vartheta_0}{V_0} \mathcal{E}_0 + \frac{c \cos \vartheta_1}{V_1} \mathcal{E}_1$$

normals has a solid angle

$$d\omega = \rho \rho' \cos^2 \vartheta \cdot r^2 d\omega'$$

so that the total amount of energy radiating from the centre may be represented by the integral

$$E = \frac{\pi^2 c^2}{2T^4} \int \left(\frac{b_{x'}^2 \tau^2}{V_{x'}^2} + \frac{b_{y'}^2 \tau^2}{V_{y'}^2} \right) d\omega.$$

It is only in the case of uniaxial crystals that this integral can be further calculated.

Geology. — "*On brackish and fresh water deposits of the river Silat in Western-Borneo.*" By Prof. K. MARTIN.

(This communication will not be published in these Proceedings).

(March 22, 1906).

KONINKLIJKE AKADEMIE VAN WETENSCHAPPEN TE AMSTERDAM.

PROCEEDINGS OF THE MEETING of Saturday March 31, 1906.

(Translated from: Verslag van de gewone vergadering der Wis- en Natuurkundige

Proceedings March 31, 1906.

E R R A T A.

p 746, line 12 from top for $x = 0.01$ read $x = 0.1$
 „ 13 „ „ „ $x = 0.02$ „ $x = 0.2$

of mixtures from those of the components. By Dr. J. E. VERSCHAFFELT. Supplement no. 11 to the Communications from the Physical Laboratory at Leiden. (Communicated by Prof. H. KAMERLINGH ONNES).

(Communicated in the meeting of January 27, 1906).

1. In the following pages I intend to show that the original equation of VAN DER WAALS

$$p = \frac{RT}{v - b_x} - \frac{a_x}{v^2}, \dots \dots \dots (1)$$

where is put

$$\left. \begin{aligned} a_x &= a_{11}(1-x)^2 + 2a_{12}x(1-x) + a_{22}x^2 \\ b_x &= b_{11}(1-x)^2 + 2b_{12}x(1-x) + b_{22}x^2 \end{aligned} \right\} \dots \dots \dots (2)$$

and where also are made the simplified suppositions¹⁾

¹⁾ Comp. KAMERLINGH ONNES and ZAKRZEWSKI, Suppl. no. 8, Proc. Sept. 24, 1904, p. 227.

$$a_{12} = \sqrt{a_{11} a_{22}} \quad , \quad b_{12} = \frac{1}{2} (b_{11} + b_{22}) \quad . \quad . \quad . \quad (3)$$

represents pretty well the special properties of mixtures. In cases where we have no observations of mixtures of two substances, the formulae given above will probably enable us to predict the properties of the mixtures of those two substances by means of the a 's and b 's — i. e. the critical elements — of the components; this circumstance might be of some use in the choice of substances whenever one wishes to observe definite phenomena in mixtures.

From formulae (1) and (3) we derive the formulae:

$$\left. \begin{aligned} \frac{T_{xk}}{\sqrt{p_{xk}}} &= \frac{T_{0k}}{\sqrt{p_{0k}}} (1-x) + \frac{T_{1k}}{\sqrt{p_{1k}}} x \\ \frac{T_{xk}}{p_{xk}} &= \frac{T_{0k}}{p_{0k}} (1-x) + \frac{T_{1k}}{p_{1k}} x \end{aligned} \right\} . \quad . \quad . \quad . \quad (4)$$

which express how the critical elements T_{xk} and p_{xk} of the mixture taken as homogeneous depend on the composition; from these formulae also follows, as we know, a linear variation of the critical volume v_{xk} . That the second of the formulae (4) agrees well with the observations has been shown by VAN DER WAALS ¹⁾. As to the course of v_{xk} , the curve denoting the variation of that quantity with x not only deviates considerably from a straight line ²⁾ (VERSCHAFFELT and KEESOM derive even from their experiments a maximum for v_{xk}) but also the quadratic formula cannot be brought to harmonize with the observations ³⁾.

Not too much importance should be attached to this deviation of a quantity so closely connected with b'); of higher import it seemed to me to investigate in how far the formulae (4) accurately represent the critical temperatures and pressures, as in connection with the law of corresponding states, of which the approximate validity may be considered to be established, these quantities entirely determine the conduct of a mixture. But also here, of course, we should not strain our expectations too high.

2. First I have computed from formulae (4) the values of the quantities:

¹⁾ Proceedings Nov. 1897.

²⁾ Comp. KAMERLINGH ONNES and REINGANUM. Comm. no. 59b, Proc. Sept. 29, 1900; BRINKMAN, Thesis for the doctorate, Amsterdam 1904, p. 73.

³⁾ Ibidem; comp. also VERSCHAFFELT, Comm. Suppl. N^o. 5.

⁴⁾ For the possible causes of that deviation comp. BRINKMAN, loc., cit., p. 75.

$$\left. \begin{aligned} \alpha &= \frac{1}{T_{0k}} \left(\frac{dT_{rk}}{dx} \right)_0 = 2 \frac{T_{1k}}{T_{0k}} \left(\sqrt{\frac{p_{0k}}{p_{1k}}} - \frac{T_{1k} p_{0k}}{T_{0k} p_{1k}} - 1 \right) \\ \beta &= \frac{1}{p_{0k}} \left(\frac{dp_{rk}}{dx} \right)_0 = 2 \frac{T_{1k}}{T_{0k}} \left(\sqrt{\frac{p_{0k}}{p_{1k}}} - \frac{p_{0k}}{p_{1k}} \right), \end{aligned} \right\} \quad (5)$$

namely for those mixtures for which the α and β had been already derived from the observations by the application of the law of corresponding states. The computed values are given in the following table; the values in brackets follow from the observations.

CO, with CH ₃ Cl	$\alpha = 0,363$ (0,378)	$\beta = -0,149$ (0,088)
CH ₃ Cl with CO,	$-0,270$ ($-0,221$)	$0,068$ (0,281)
CO, with H ₂ ,	$-0,978$ ($-1,219$)	$-0,439$ ($-1,645$)
CO, with O ₂ ,	$-0,513$ ($-0,6563$)	$-0,242$ ($-1,0871$)

Of principal importance are here the signs of the α and β , and in this respect there is a good agreement, when we except the β for CO, with CH₃Cl; I must remark, however, that from the experiments of BRINKMAN a negative β is derived for this mixture¹⁾.

3. With the derived values of α and β we now, using the formulae constructed by KESOM and me, might compute the quantities $\left(\frac{dT_{xpl}}{dx} \right)_0$, $\left(\frac{dp_{xpl}}{dx} \right)_0$ and others; but as our principal concern is the signs of those quantities, it is superfluous to perform these computations. In fact, we immediately obtain a survey of the properties of the mixtures with a small proportion of one of the components when we draw the values of α and β as I have done before²⁾; this time of course in a diagram, based no longer on the empirical equation of state used then, but on equation (1). It is still easier, by means of the formulae given in Comm. Suppl. n°. 5 (Proceedings May 30, 1903) to express the α and β in KORTHEWEG's³⁾ κ and γ , and then to use his diagram which, as is known, is based on the original equation of state. Thus we find that the points (α, β) — or (κ, γ) — lie exactly in the fields which correspond to the properties of the mixtures; here also, therefore, the investigation has a favourable result.

4. I shall now communicate some computed values of T_{rk} and p_{rk} for the mixtures under consideration, and compare them with the values derived from the observations. (See following table).

¹⁾ Loc. cit., p. 73; comp. also the table on the following page.

²⁾ Comm. Suppl. no. 6, Proc. 30 May 1903.

³⁾ Proc. 31 Jan. 1903.

CH ₃ Cl—CO ₂ (BRINKMAN)				
	Computed		Observed	
	T_{sk}	p_{sk}	T_{sk}	p_{sk}
$x = 0$ (pure CH ₃ Cl)	416.2	65.93	416.16	65.93
$\frac{1}{4}$	402.1	66.54	398.56	65.73
$\frac{1}{2}$	388.1	67.20	384.26	66.89
$\frac{3}{4}$	360.0	68.74	351.88	69.19
$\frac{4}{4}$	332.2	70.70	324.96	71.06
$x = 1$ (pure CO ₂)	304.2	73.10	304.16	73.10

CO ₂ —H ₂ (VERSCHAFFELT)				
$x = 0$ (pure CO ₂)	304.7	73.6	304.7	73.6
0.05	289.9	72.0	287.8	68.1
0.01	275.2	70.2	273.6	63.5
0.02	245.7	66.4	248.7	54.8
$x = 1$ (pure H ₂)	38.5	20	38.5	20

CO ₂ —O ₂ (KEESOM)				
$x = 0$ (pure CO ₂)	304.02	72.93	304.02	72.93
0.1	288.6	71.17	285.68	67.70
0.2	273.0	69.24	272.92	67.30
$x = 1$ (pure O ₂)	154.2	50.7	154.2	50.7

HCl—C ₂ H ₆ (QUINT)				
$x = 0$ (pure HCl)	324.3	84.13	324.3	84.13
0.1318	318.6	76.44	315.5	77.3
0.4035	310.9	64.59	303.0	65.5
0.6167	307.2	57.75	299.4	58.6
0.7141	306.2	55.17	298.8	55.7
$x = 1$ (pure C ₂ H ₆)	304.9	48.94	304.9	48.94

On the whole the computed course of the T_{sk} and p_{sk} agrees fairly well with the observations. The only important discrepancy is that from the observations of mixtures of HCl and C₂H₆, there follows a minimum for the critical temperature, while the computation would not have predicted this circumstance. This minimum, however, is not

very strongly pronounced; therefore I have investigated whether perhaps the computation had predicted it for mixtures of N_2O and C_2H_6 , for which the minimum critical temperature is probably much lower than that of the components. I really find on the side of ethane, the component with the lowest critical temperature, $\alpha = -0.019$, hence a negative value, which renders the existence of a minimum critical temperature necessary.

5. After having shown by means of these few instances the usefulness of formulae (4) for our purpose, I shall now closely examine the course of the critical lines, in order thence to deduce which conditions must be fulfilled by the critical elements of the components, in order that the mixtures may show definite phenomena.

The shapes of these curves in the pT diagram have been deduced by VAN DER WAALS from formulae (1) and (2)¹⁾ with the single simplification $b_{12} = \frac{1}{2}(b_{11} + b_{22})$. What we shall find here will therefore be a special case of the more general forms found by VAN DER WAALS, namely the transition between the two cases $a_{11}^2 > a_{11} a_{22}$ and $a_{11}^2 < a_{11} a_{22}$, investigated by him.

If we put $\tau = \frac{T_{xk}}{T_{ok}}$ and $\pi = \frac{p_{xk}}{p_{ok}}$ and moreover introduce the new variable $z = \sqrt{\pi}$, we may in our case write the equation of the critical line:

$$z^2 \tau_1 (\sqrt{\pi_1} - 1) - z\tau (\pi_1 - \tau_1) + \tau (\pi_1 - \tau_1 \sqrt{\pi_1}) = 0. \quad (6)$$

In the $z\tau$ diagram therefore the critical line is a portion of a hyperbola (see fig. 1), except when $\pi_1 = \tau_1$, for then it is a portion of a parabola (represented in fig. 1 by OAB ; a straight line in the pT diagram), and when $\pi_1 = 1$ or $\sqrt{\pi_1} = \tau_1$, for then it is a straight line (CD and OE).

In our drawing (fig. 1) one of the components always lies at the point A , and we see that the form of the critical line is only determined by the relations $\frac{T_{1k}}{T_{ok}}$ and $\frac{p_{1k}}{p_{ok}}$. Besides, when we move the second component along one of the critical lines, the shape of that line remains unchanged.²⁾

Fig. 1 therefore represents the forms which the critical line can adopt in our case. In order to show that the observed forms agree with these in a satisfactory way, I have drawn in the same figure 1 the critical lines derived from the observations. The lines for

¹⁾ Versl. Kon. Akad. Nov. 1897.

²⁾ As VAN DER WAALS (loc. cit.) has remarked in general.

mixtures of CO_2 with CH_4 , Cl and of HCl with C_2H_6 , are drawn twice in it, one time with the one component, the other time with the other component at A . Of the lines for mixtures of carbon dioxide with hydrogen or oxygen we could draw only a small portion in the neighbourhood of carbon dioxide (point A).

These critical lines fit into the system of curves in a satisfactory way, except the line $\text{CO}_2\text{—O}_2$. Also the beginning of the line $\text{CO}_2\text{—H}_2$ fits well into the diagram, but its further portion, if it is to terminate at the point H_2 , cannot but deviate strongly from it.

6. The drawing of fig. 1 enables us also to determine how we must choose the pure mixtures in order that the mixtures may possess definite properties. VAN DER WAALS (loc. cit.) has pointed out the circumstance that the course of the critical lines (even when $a_{11} > a_{11} a_{22}$) excludes the existence of a maximum critical temperature or of a maximum or minimum critical pressure. Yet mixtures occur which show ¹⁾ a minimum critical temperature, and in our case we find as conditions for its existence ²⁾:

$$\pi_1 + \tau_1 > 2 \tau_1 \sqrt{\pi_1} \text{ and also } > 2 \sqrt{\pi_1}.$$

The area, within which the second component must lie, if the critical temperature is to reach a minimum for one of the mixtures, is therefore bounded by the two curves

$$\tau = 2z - z^2 \text{ and } \tau = \frac{z^2}{2z - 1},$$

represented in fig. 1 by OAF and GAH respectively. The first line is one of the critical lines, namely that which has a vertical tangent at a ; the other contains all the points of the critical lines where the tangent is vertical. It may be easily seen that the second component must lie between those two curves, i. e. in the fields 2 and 3. On the strength of this we may predict that in general a minimum critical temperature will be observed when the critical

¹⁾ The elements of the mixture for which the critical temperature is minimum, are here determined by:

$$z_{mt} = 2 \frac{\pi_1 - \tau_1 \sqrt{\pi_1}}{\pi_1 - \tau_1}, \quad \tau_{mt} = 4 \tau_1 \frac{(\sqrt{\pi_1} - 1)(\pi_1 - \tau_1 \sqrt{\pi_1})}{(\pi_1 - \tau_1)^2},$$

$$a_{mt} = \sqrt{\pi_1} \frac{(\pi_1 + \tau_1 - 2\tau_1 \sqrt{\pi_1})}{(\sqrt{\pi_1} - \tau_1)(\pi_1 - \tau_1)}.$$

²⁾ The general conditions for the existence of a minimum critical temperature are given in the Molecular Theory of VAN DER WAALS.

temperatures of the components differ little and the critical pressures differ relatively much. It is known that experience confirms this conclusion.

7. Now I shall try to find how the substances must be chosen in order that one of the mixtures near the critical circumstances may show a maximum — or a minimum — vapour pressure. At the critical point (at the same time plaitpoint) of that mixture we then have, along the critical line, $\frac{T_{xk}}{p_{xk}} \frac{dp_{xk}}{dT_{xk}} = \left(\frac{\partial p}{\partial t} \right)_k$.

As we have based our speculations on the original equation of state of VAN DER WAALS, we must, strictly taken, use for $\left(\frac{\partial p}{\partial t} \right)_k$ the value which follows from this equation, i. e. 4. Thus we find¹⁾ that the area within which the second component must lie, is bounded by the curves :

$$\tau = \frac{1}{2} (3z - z^2) \text{ and } \tau = \frac{2z^2}{3z-1}, ^2)$$

represented by *OAI* and *KAL* respectively in fig. 1. *KAL* is again the critical line which shows at the point *A* itself the property mentioned above, while *OAI* combines all the points where $\frac{\tau}{\pi} \frac{d\pi}{d\tau} = 4$ or $\tau z \frac{dz}{d\tau} = 2$. The second component must be situated between these two lines, namely in field 3 or 4.

We may repeat that in order to observe the property under consideration, the pure substances must be chosen so that the critical temperatures differ little, but the values of the critical pressures differ relatively much; however, the component with the higher critical temperature must also have the higher critical pressure³⁾.

¹⁾ The elements of the mixture, of which the vapour pressure is maximum or minimum, are given by

$$\alpha_{mp} = \frac{2\pi_1 \sqrt{\pi_1 + \tau_1} \sqrt{\pi_1 - 3\tau_1\pi_1}}{2(\pi_1 - \tau_1)(\sqrt{\pi_1 - \tau_1})}, \quad z_{mp} = 3 \frac{\pi_1 - \tau_1 \sqrt{\pi_1}}{\pi_1 - \tau_1},$$

$$\tau_{mp} = \frac{9}{2} \tau_1 \frac{(\sqrt{\pi_1 - 1})(\pi_1 - \tau_1 \sqrt{\pi_1})}{(\pi_1 - \tau_1)^2}.$$

²⁾ The general conditions for the existence of a maximum or a minimum vapour pressure have been derived by VAN DER WAALS (Versl. Kon. Ak. 1895/96).

My quotation of VAN LAAR in the Dutch edition (same note) resulted from a misunderstanding.

³⁾ The latter does not always hold good, as for instance with mixtures of CO_2 and C_2H_6 (KUENEN, Zeitschr. f. physik. Chem., 24, 681, 1897).

Hence a minimum critical temperature and a maximum vapour pressure are two phenomena which as a rule occur together, but not necessarily; this is only the case in field 3.

From fig. 1 it appears that, according to our reasoning, only a maximum vapour pressure is possible; yet we know that there are mixtures which show a minimum vapour pressure, and it has been proved by KUENEN¹⁾ that this phenomenon occurs even under the critical circumstances. Here it seems that there is a fundamental deviation from the observation. Nevertheless it is remarkable that the mixtures which show a minimum vapour pressure are always of such kind that at least one of the components is an anomalous substance²⁾; so that there is reason to suppose that with mixtures of normal substances a minimum vapour pressure never occurs; and our speculations, which are based on the law of corresponding states, are applicable to normal substances only.

8. Starting from the same suppositions as set forth here, VAN LAAR³⁾ has found an accurate expression for the projection of the plaitpoint line on the vx -plane. I have tried to derive from this the equation of the plaitpoint line in the pT — hence also in the $z\tau$ — diagram⁴⁾, but without success. Without therefore occupying myself further with the general form which the plaitpoint line in our case takes in the $z\tau$ -diagram, I shall investigate a few points, namely the occurrence of a maximum or a minimum plaitpoint temperature, and that of a maximum or a minimum plaitpoint pressure.

According to KEESOM's⁵⁾ formulae (2a) and (2b) we have

$$\left. \begin{aligned} \frac{1}{T_{ok}} \left(\frac{dT_{xpl}}{dx} \right)_0 &= \frac{\tau_1}{4\pi_1^2} [\tau_1 (3\sqrt{\pi_1} - 1)^2 - 4\pi_1 \sqrt{\pi_1}] \\ \frac{1}{p_{ok}} \left(\frac{dp_{xpl}}{dx} \right)_0 &= \frac{1}{\pi_1^2} [\tau_1^2 (3\sqrt{\pi_1} - 1)^2 - 2\pi_1 \tau_1 (5\sqrt{\pi_1} - 1) + 4\pi_1^2] \end{aligned} \right\} \quad (7)$$

Hence follows that the boundary between $\frac{dT_{xpl}}{dx} > 0$ and $\frac{dT_{xpl}}{dx} < 0$ is formed by the curve:

¹⁾ Arch. Néerl., (2), 5, 306, 1900 (Livre jubilaire de H. A. LORENTZ).

²⁾ For the bibliography of this cf. HARTMAN, Thesis for the doctorate, page 84, Leiden 1899.

³⁾ Proceedings April 22, 1905.

⁴⁾ By eliminating x and v between the equation of the vx projection of the plaitpoint line, the equation of the spinodal surface (VAN LAAR's formula 6, loc. cit.), and the equation of state.

⁵⁾ Communication no. 75, Proceedings Dec. 28, 1901.

$$\tau = \frac{4z^3}{(3z-1)^2}, ^1)$$

represented in fig. 2 by the branches *BAC* and *OD*; to the left of it $\frac{dT_{xpl}}{dx} < 0$, to the right > 0 . If in consequence we take *A* as the component with the lower critical temperature, in other words: if we put $\tau_1 > 1$, there must be a minimum plaitpoint temperature when the second component lies in the area *AGCABDHA*; in general this will again occur when the critical temperatures differ little, whereas the critical pressures differ much²⁾. This does not prove, however, that there may not be other circumstances for which the plaitpoint temperature reaches a minimum.

If on the other hand we take *A* as a component with the higher critical temperature, there must be a maximum plaitpoint temperature when the second component lies in the area *OHK*.³⁾ Neither here is it proved that the phenomenon is restricted to that area.

9. The boundary between $\frac{dp_{xpl}}{dx} > 0$ and $\frac{dp_{xpl}}{dx} < 0$ is formed by the curve

$$\tau^3 (3z-1)^2 - 2\tau z^3 (5z-1) + 4z^4 = 0,$$

represented in fig. 2 by *EAF*; $\frac{dp_{xpl}}{dx}$ is negative within that line and positive beyond it. Whence follows that a minimum plaitpoint pressure is impossible, at least little probable, while a maximum plaitpoint pressure must occur when the second component lies within the area *ALEAF* τ *OMA*; this will therefore in general be the case when the critical temperatures differ much, which is confirmed by experiment.

10. Finally, in order to show by means of an example that the suppositions whence we started in the main represent precisely the

¹⁾ Cf. also VAN LAAR, loc. cit., p. 585.

²⁾ This is again the same condition as for the existence of a minimum critical temperature; but as $\frac{1}{T_{ok}} \left(\frac{dT_{xpl}}{dx} \right)_0 = \alpha + \frac{1}{16} (\beta - 4z)^2$, $\frac{dT_{xpl}}{dx}$ may be positive with negative α , in other words: a minimum plaitpoint temperature requires a minimum critical temperature, but not reversely. This may also be seen from fig. 2, where I have once more drawn the line *GAH* of fig. 1 (dotted line).

³⁾ An instance of this is probably not to be found.

course of the plaitpoint elements, I shall give here the results of a computation which I have executed for CO_2 and H_2 .

$x = 0$ (pure CO_2)	$T_{xpl} = 304,1$	$p_{xpl} = 72,9$
0,1	295,8	90,8
0,2	287,4	108,7
0,3	274,8	124,8
0,4	260,4	140,0
0,5	244,3	153,9
0,6	222,1	162,9
0,7	194,0	164,5
0,8	157,0	152,5
0,9	108,8	115,2
$x = 1$ (pure H_2)	38,5	20

The course of the plaitpoint line resulting from this agrees with fig. 9, plate I of HARTMAN'S Thesis for the doctorate; in reality, however, the maximum of the plaitpoint pressure will lie much higher.

Physics. — "*Appendix to Communication N°. 81*". (Proceedings June 28 and September 27, 1902) and Supplement N°. 7 (Proceedings Oct. 31, 1903). By Dr. J. E. VERSCHAFFELT. Supplement N°. 12 to the Communications of the Physical Laboratory at Leiden. (Communicated by Prof. H. KAMERLINGH ONNES).

(Communicated in the meeting of January 27, 1906).

In the expression which I have given before (Comm. N°. 81 and also Suppl. N°. 7) for the function ψ in the neighbourhood of the plaitpoint an inaccuracy has remained. I have found that I have neglected therein more than a mere linear function of x .

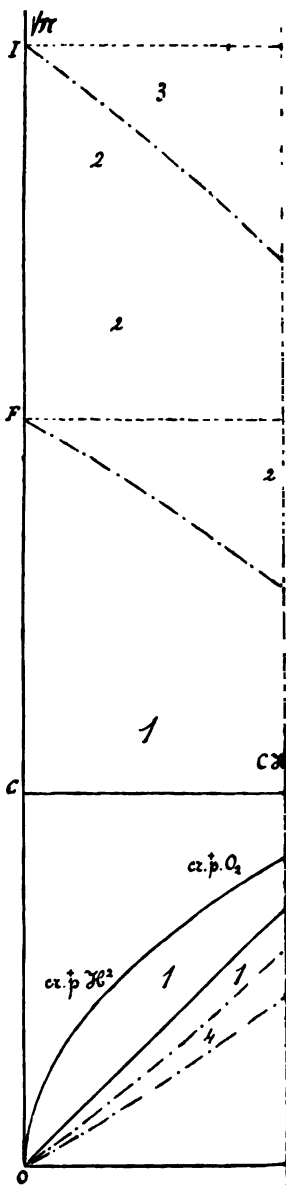
If we write:

$$\psi = \int_v^V p dv + \psi_V,$$

where V represents a very large volume, then ψ_V is the free energy in the perfect gaseous state, with the exception of an error which will be smaller as V itself becomes larger, and which vanishes when we put $V = \infty$.

The first term of ψ , which depends on v , may be dissolved in the following way:

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$$\int_v^V p dv = \int_v^{v_{Tk}} p dv + \int_{v_{Tk}}^V p dv.$$

The first part I have developed before, and $X = \int_{v_{Tk}}^V p dv - RT \log V$

($V = \infty$) is the x -function which has then been wrongly left out of account. This function cannot be developed in the same manner as the first integral, because the series used for that is no longer convergent for large volumes; we must therefore turn to KAMERLINGH ONNES' empirical equation of state.

When this equation of state is written in a reduced form, it also represents the reduced equation of the isothermal of the mixture x , at the reduced temperature $t = \frac{T}{T_{xk}}$, so that

$$\begin{aligned} \int_{v_{Tk}}^V p dv &= p_{xk} v_{xk} \int_{\frac{v_{Tk}}{v_{xk}}}^{\frac{V}{v_{xk}}} p dv = \\ &= RT (\log V - \log v_{Tk}) - \frac{\mathfrak{B}}{\lambda^2} p_{xk} v_{xk}^3 \left(\frac{1}{V} - \frac{1}{v_{Tk}} \right) - \frac{\mathfrak{C}}{\lambda^2} p_{xk} v_{xk}^3 \left(\frac{1}{V^2} - \frac{1}{v_{Tk}^2} \right). \end{aligned}$$

Hence the neglected x -function is:

$$X = -RT \log v_{Tk} + \frac{\mathfrak{B}}{\lambda^2} \frac{p_{xk} v_{xk}^3}{v_{Tk}} + \frac{1}{2} \frac{\mathfrak{C}}{\lambda^2} \frac{p_{xk} v_{xk}^3}{v_{Tk}^2} + \dots$$

and this may be developed again:

$$X = X_0 + X_1 (x - x_{Tk}) + X_2 (x - x_{Tk})^2 + \dots$$

where the co-efficients X_0 , X_1 , X_2 , etc. are still functions of temperature. Fortunately the neglect of that function X has not influenced the results in first approximation; however in the formulæ 4, 5, 12 and 13 of suppl. N°. 7 we have to add $2 X_1$ to the factor

$$\frac{RT}{x_k(1-x_k)}.$$

Mathematics. — “*A particular series of quadratic surfaces with eight common points and eight common tangential planes.*”

By Prof. P. H. SCHOUTE.

1. “In our space are given a fixed line and four projectively related plane pencils of rays. To be found the common transversals of the fixed line and a set of four corresponding rays.”

Notation ¹⁾. We indicate the fixed line by l^0 , the vertices and planes of the pencils of rays by O_1, O_2, O_3, O_4 and $\alpha_1, \alpha_2, \alpha_3, \alpha_4$, four corresponding rays and their two transversals by l_1, l_2, l_3, l_4 and l, l' , the pencils of rays themselves by $(l_1), (l_2), (l_3), (l_4)$ and the pairs of points of intersection of l, l' with each of the rays l_1, l_2, l_3, l_4 by $(S_1, S'_1), (S_2, S'_2), (S_3, S'_3), (S_4, S'_4)$. Farther the symbols $l_{1,2}, l_{1,3}, \dots, l_{1,4}$ may represent the lines of intersection of the pairs of planes $(\alpha_1, \alpha_2), (\alpha_1, \alpha_3), \dots, (\alpha_3, \alpha_4)$.

2. The order of the locus of the pair of transversals l, l' is easy to deduct from its section with α_1 , which consists of two parts: the locus $[(S_1, S'_1)]$ of the pair of points (S_1, S'_1) and some generating transversals. Each ray l_1 of the pencil (l_1) containing a single pair of points (S_1, S'_1) , the locus $[(S_1, S'_1)]$ is an hyperelliptic curve the order of which exceeds the number of times a transversal passes through O_1 by two. Now three transversals pass through O_1 . By projecting the pencils $(l_2), (l_3)$ out of O_1 on α_1 we find namely in α_1 three projectively related pencils $(l'_2), (l'_3), (l'_4)$ and now three times three corresponding rays l'_2, l'_3, l'_4 pass through one and the same point, the conics generated by the pairs $[(l'_2), (l'_4)]$ and $[(l'_3), (l'_4)]$ having besides O_1 three more points in common. So the locus $[(S_1, S'_1)]$ is a curve c_1^5 of order five having in O_1 a threefold point; its genus is three. Now that three transversals pass through O_1 there must be according to the principle of duality also three generating transversals in α_1 . And indeed, the pencils $(l_2), (l_3), (l_4)$ do describe on the lines $l_{1,2}, l_{1,3}, l_{1,4}$ three projectively related series of points $(A_2), (A_3), (A_4)$ where three times three corresponding points A_2, A_3, A_4 lie on the same right line α , the conics generated by the pairs $[(A_2), (A_4)]$ and $[(A_3), (A_4)]$ possessing three more common tangents besides $l_{1,4}$. So the total section of α_1 with the locus of the pair of transversals l, l' is a system of order eight and this locus itself a scroll O^8 with a nodal curve of order eighteen. The order of the nodal curve ensues even from the fact that the surface O^8 must correspond in genus to c_1^5 ; moreover

¹⁾ For notation and reasoning see a former communication.

the eighteen points of intersection of the curve with α_1 are easy to indicate.

The obtained surface O^8 is intersected by the given line l^0 in eight points. So in general there are eight lines resting on l^0 and on four corresponding rays l_1, l_2, l_3, l_4 .

3. In the preceding we have assumed that four corresponding rays l_1, l_2, l_3, l_4 always admit of two common transversals, not taking into account the possibility that four corresponding rays have an hyperboloidic position. In the general case this singularity does not occur; for the condition that four lines are situated hyperboloidically is a *threefold* one and the number of corresponding quadruplets of rays is only *singly infinite*. However, this does not prevent a proper selection of the data from leading to projectively related pencils with a quadruplet of corresponding rays lying hyperboloidically; to this end we have but to assume the points O_1, O_2, O_3, O_4 on four hyperboloidic lines l'_1, l'_2, l'_3, l'_4 and the planes $\alpha_1, \alpha_2, \alpha_3, \alpha_4$ through these same lines, and to fix the projective correspondence in such a way that these four lines correspond.

If the case of four hyperboloidic rays l'_1, l'_2, l'_3, l'_4 really occurs, the scroll O^8 of the lines intersecting these four rays belongs to the locus under consideration; we have thus further to investigate whether this O^8 joins the surface O^8 of the general case or whether this surface breaks up in this special case into the surface O^8 and a completing surface O^6 . At the outset only the first possibility occurred to me and I contented myself with developing grounds why this elevation of the order of the locus from eight to ten need not really clash with the wellknown principle of the conservation of the number¹⁾.

Although at first sight it seems rather absurd that the infinitesimal small difference between four *nearly* and four *perfectly* hyperboloidic rays should rule the locus obtained by means of the remaining quadruplets so as to let us find in the first case an O^8 and in the second an O^6 , yet as will be proved directly the second of the two suppositions mentioned above is the right one, not the first; so in that sense this paper has had to be modified.

The surface O^8 of the common transversals of any hyperboloidic quadruplet l'_1, l'_2, l'_3, l'_4 contains these lines and so it must admit of a transversal through each of the vertices O_1, O_2, O_3, O_4 and in each of the planes $\alpha_1, \alpha_2, \alpha_3, \alpha_4$. The deduction of the order of the locus O^8 has shown that through each of the four points O three

¹⁾ See for this a corresponding case of apparent contradiction in my "Mehrdimensionale Geometrie", vol. I, page 263.

transversals pass and likewise there are three in each of the four planes α . Hence the question, whether besides the scroll O^3 a surface O^8 or a surface O^6 presents itself, can be decided by the fact whether the four generators through the points O and the four generators in the planes α are common to the two parts of the locus or not. Now, as a matter of fact, those two parts can have but two generators in common, viz. those two common transversals of l'_1, l'_2, l'_3, l'_4 , joining the preceding pairs of transversals and the following of the adjacent quadruplets. So the eight indicated transversals of l'_1, l'_2, l'_3, l'_4 , are not situated on the other part of the locus and consequently the latter is cut by each of the planes α_i according to a curve c^4 with a node in O_i and two right lines; so the remaining part is a surface O^6 with a nodal curve of order nine. For the scroll O^3 of genus three appears instead a combination of a regulus O^3 and a scroll O^4 of genus one cutting each other in two right lines and a twisted curve of order ten.

From the preceding follows immediately what will happen when the singularity of the hyperboloidic quadruplet presents itself more than once. If two of those particular quadruplets are at hand O^8 breaks up into three parts, two quadratic reguli and a scroll O^4 with a twisted cubic as nodal curve; so the latter principal component part of the locus is of genus zero and has with each of the two quadratic surfaces two generating transversals and a twisted curve of order six in common. If the projectively related pencils contain three hyperboloidic quadruplets O^8 breaks up into four quadratic reguli, three of which answer to these quadruplets whilst the fourth, really the locus, is supplied by all the remaining quadruplets; the latter surface is intersected by each of the others according to the edges of a skew quadrilateral, whilst these three intersect each other in general according to twisted curves of order four. And if there are four hyperboloidic quadruplets, as will appear later on, all quadruplets are situated hyperboloidically; then the case presents itself where the order of the locus, so far always eight, becomes infinite.

4. The following simple example will show that it is not difficult to choose the data so as to allow *each* quadruplet of corresponding rays to lie hyperboloidically.

We imagine the four pencils $(l_1), (l_2), (l_3), (l_4)$ situated in the four sides of a cube (fig. 1), we assume the vertices O_1, O_2, O_3, O_4 of the pencils in the centres of these sides and we allow those rays l_1, l_2, l_3, l_4 to correspond which form the same angle φ with their

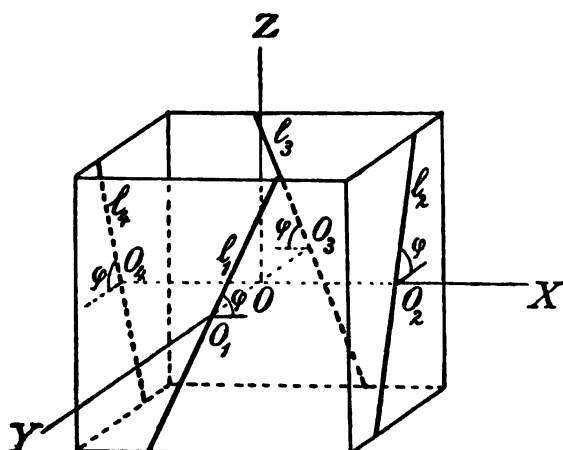


Fig. 1.

projections on the plane through the four vertices when one keeps in the same direction. To each quadruplet of corresponding rays belongs a hyperboloid of revolution with OZ for axis and circle $O_1O_2O_3O_4$ as minimal circle ("cercle de gorge"), whilst the hyperboloids of revolution belonging to the various values of φ , touching each other according to that circle, form a tangential pencil as well as an ordinary one. Each of those surfaces presents itself twice as bearer of two reguli corresponding to two supplementary values of φ . In this case is a rule what was an exception above; here the number to be found is infinite, as two lines satisfying the conditions pass through each point of l^p , the two generators of the surface of this peculiar pencil passing through this point. Indeed, the case of an infinite number of solutions makes its appearance even as soon as there is only one hyperboloidic quadruplet and l^p is at the same time director ray of the regulus determined by this quadruplet as director rays; then through each point of l^p passes only one line satisfying the question.

To simplify the representation the preceding particular case has been taken on purpose as regularly as possible. The principal thing is what the figure retains after a projective transformation, that namely the vertices O_1, O_2, O_3, O_4 lie in the same plane, that the planes $\alpha_1, \alpha_2, \alpha_3, \alpha_4$ pass through the same point and that all quadratic surfaces touch those planes in the vertices mentioned above; the regular situation of the four vertices on the common minimal circle is of secondary importance.

This leads us to a new question, viz. whether it is impossible to find four projectively related pencils of rays where each quadruplet of

corresponding rays has hyperboloidic position, the vertices not lying in the same plane, the bearing planes not passing through the same same point and those planes not being touched in those vertices by all quadratic surfaces herewith generated. Analytically as well as geometrically we can convince ourselves in a simple way of the reverse.

With respect to a rectangular system of coordinates $O(XYZ)$ the four pairs of equations.

$$\left. \begin{matrix} y = px + q \\ z = rx + s \end{matrix} \right\}, \quad \left. \begin{matrix} -y = px + q \\ -z = rx + s \end{matrix} \right\}, \quad \left. \begin{matrix} y = -px + q \\ -z = -rx + s \end{matrix} \right\}, \quad \left. \begin{matrix} -y = -px + q \\ z = -rx + s \end{matrix} \right\}$$

represent four lines l_1, l_2, l_3, l_4 with hyperboloidic position. For the conditions under which the surface

$$ax^2 + by^2 + cz^2 = 1$$

contains one of those lines are

$$a + bp^2 + cr^2 = 0, \quad bpq + crs = 0, \quad bq^2 + cs^2 = 1,$$

any of the four lines being taken. Now these lines l_1, l_2, l_3, l_4 hang together in such a way, that by a rotation of 180°

round the axis OX the lines l_1 and l_2 and likewise the lines l_3 and l_4 pass into each other.

" " " OY " " l_1 " l_3 " " " " l_2 " l_4 " " " "

" " " OZ " " l_1 " l_4 " " " " l_2 " l_3 " " " "

If now in a plane α_1 the line l_1 describes a pencil of rays with O_1 as vertex, the lines l_2, l_3, l_4 will describe the pencils obtained by making the pencil (l_1) undergo a rotation of 180° round the axes OX, OY, OZ , where the four vertices O_1, O_2, O_3, O_4 will not lie in the same plane, and the bearing planes will not pass through the same point. And then is also excluded that the planes $\alpha_1, \alpha_2, \alpha_3, \alpha_4$ are touched in O_1, O_2, O_3, O_4 by the generated quadratic surfaces. For two quadratic surfaces touching each other in four points not situated in one and the same plane coincide and the surfaces under consideration do not.

Let us consider geometrically a more special case connected with a regular tetrahedron. We start from a cube and take (fig. 2) one of the two groups of four not adjacent vertices A_1, A_2, A_3, A_4 as vertices of this tetrahedron. Then the faces $A_1, A_2, A_3, A_4, A_1, A_2, A_3, A_4, A_1, A_2, A_3, A_4$ of this tetrahedron are the bearing planes $\alpha_1, \alpha_2, \alpha_3, \alpha_4$, the centres of those equilateral triangles are the vertices O_1, O_2, O_3, O_4 of those pencils. And the rays l_2, l_3, l_4 corresponding to an arbitrary ray l_1 of the first pencil are found again by a rotation of 180° round the lines OX, OY, OZ through the centre of the cube parallel to the edges of the cube, which are at the same time the connecting lines EE', FF', GG' of centres of pairs of opposite edges of the

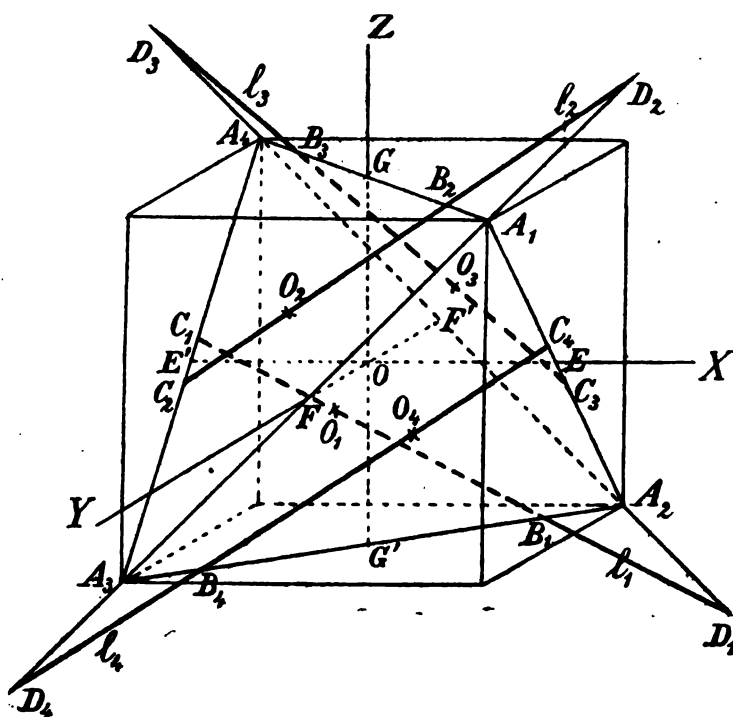


Fig. 2

tetrahedron. From a simple inspection of the figure appears that the three points, in which any of the faces of the tetrahedron is cut by the corresponding three rays lying in the other faces, are situated on the second asymptote of the hyperbola passing through the three vertices of that face and having the fourth corresponding ray lying in that face as an asymptote. So this ensues inter alia for the face $A_1A_2A_3$, from the three relations:

$$A_1C_2 = C_1A_2, \quad A_1D_3 = D_1A_3, \quad A_1B_4 = B_1A_4.$$

So already four lines rest on l_1, l_2, l_3, l_4 , namely one in each face, which proves that the lines l_1, l_2, l_3, l_4 have hyperboloidic position.

6. We leave our original problem for an other moment in order to investigate first the series of quadratic surfaces furnished in the last special case under consideration by the quadruplets of corresponding rays. All these surfaces have eight points in common, the four vertices O_1, O_2, O_3, O_4 of the pencils and the four points O_5, O_6, O_7, O_8 symmetric to these with respect to the common centre O ; so they belong to the net N_p of the quadratic surfaces determined by seven of those eight base-points O_i , forming in their turn the vertices of a cube. We can likewise point out eight common

tangential planes, the four planes $\alpha_1, \alpha_2, \alpha_3, \alpha_4$ of the pencils of rays and the planes $\alpha_5, \alpha_6, \alpha_7, \alpha_8$ parallel to the former and symmetric to these with respect to O ; so those quadratic surfaces are a part of the tangential net N_t determined by seven of those eight base-planes α_i , enclosing together a regular octahedron. So our series of surfaces being formed by the surfaces common to N_p and N_t , can be regarded as the intersection of those nets.

The tetrahedron of which the origin O and the points $X_\infty, Y_\infty, Z_\infty$ at infinity of the axes of coordinates are the vertices is common polar tetrahedron of all surfaces of the two nets N_p and N_t . In connection with this N_p has instead of a single infinite number of cones six pairs of planes, a pair through each of the edges of the tetrahedron, and N_t contains instead of a single infinite number of surfaces reduced to conics six pairs of points, a pair on each of the edges of the tetrahedron. So we find the most general projective transformation of the series common to N_p and N_t , by starting from an arbitrary tetrahedron, an arbitrary point and an arbitrary plane through this point and by then representing to ourselves the surfaces having the given tetrahedron as polar tetrahedron, passing through the given point and touching the given plane.

We prepare the deduction of the three characteristic numbers of our series of surfaces by determining the locus of the points of contact with one of the eight base-planes, say α_1 . By considering the indicated relation

$$A_1C_2 = C_1A_4, \quad A_1D_2 = D_1A_4, \quad A_1B_2 = B_1A_4,$$

between the two lines l_1 and l'_1 (fig. 3), in which α_1 is cut by the quadratic surface belonging to l_1 , we find immediately that B_1, C_1, D_1 on A_1A_2, A_1A_3, A_1A_4 describe projective series of points when l_1 rotates round O_1 and that l'_1 envelops a conic described in triangle

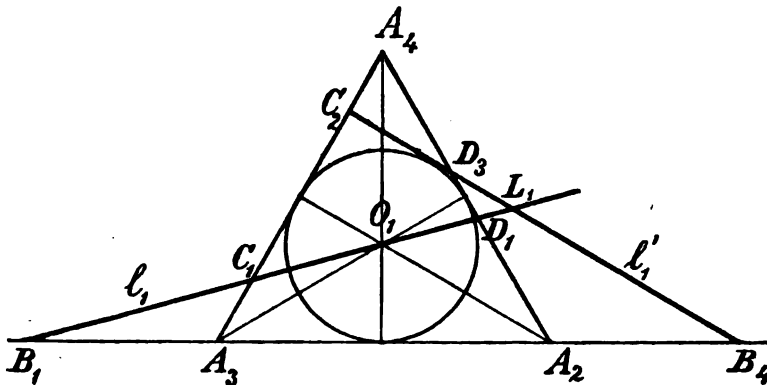


Fig. 3

$A_1A_2A_3$; by determining for each of the pairs of projective series of points on each of the bearers the point corresponding to the point of intersection of the bearers reckoned to belong to the other series it becomes evident that this conic touches the sides in the centres, so that it is the inscribed circle c^2 . The point of contact being the point of intersection L_1 of l_1 and l'_1 , the locus of this point is at the same time the locus of the point of intersection of the corresponding rays of the pencil (l_1) of order one and the pencil $(l'_1)^2$ of order two formed by the tangents l_1 of c^2 , thus a curve c^3 of order three with O_1 as node and the tangents from O_1 to c^2 , i.e. the isotropic lines through O_1 as nodal lines. This curve represented in fig. 4 touches the sides of the triangle $A_1A_2A_3$ in the centres and has the points at

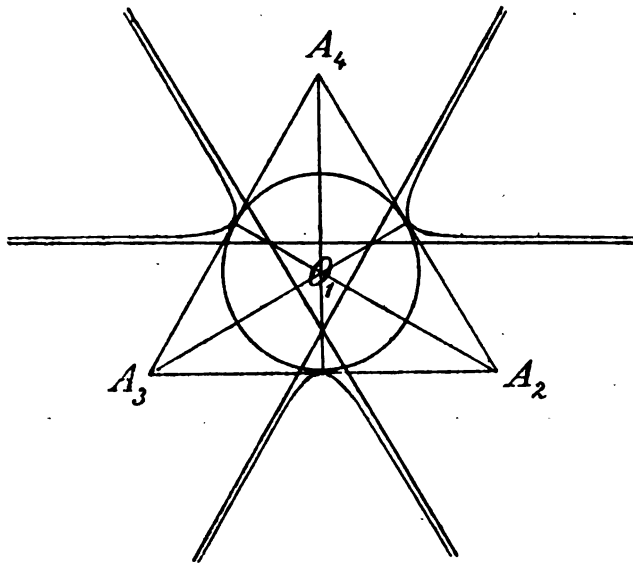


Fig. 4

infinity of the sides as inflectional points; the inflectional asymptotes run parallel to the sides at distances of four ninths of the height. In normal coordinates its equation with respect to triangle $A_1A_2A_3$ is

$$\sum x_i^2 (x_i + x_j) - \sum x_i^2 = x_1 x_2 x_3,$$

whilst the Plücker numbers are

$$\begin{aligned} n &= 3, & d &= 1, & c &= 0, \\ m &= 4, & t &= 0, & i &= 3. \end{aligned}$$

As is known we mean by the three characterizing numbers of a simple infinite series of surfaces the numbers μ, ν, ρ indicating successively how many surfaces of the series pass through any given

point, touch any given line, touch any given plane. From the following will be evident that in our case these numbers are 3, 6, 3.

All the surfaces of the net N_p with the eight base-points O_i , passing moreover through any ninth point O_n , form a pencil with O as common centre and OX, OY, OZ as common axes. Each surface of that pencil touching one of the eight base-planes α_i touches them all, so it belongs to the series. A pencil of quadratic surfaces containing three surfaces touching a given plane, we find $\mu = 3$.

All surfaces of the net N_t with eight base-planes α_i , touching moreover an arbitrary ninth plane α_n , form a tangential pencil with O as common centre and OX, OY, OZ as common axes. Each surface of that tangential pencil passing through one of the eight base-points O_i , contains all these, so it belongs to the series. So $\rho = 3$, as three surfaces of a given tangential pencil pass through a given point.

The number of surfaces of the series touching an arbitrary line of the plane A, A, A , is three, because this line cuts the locus of the points of contact (fig. 4) in three points. As the line is assumed in a common tangential plane, each of those three cases counts twice; so $\nu = 6$, as is immediately confirmed analytically.

So the indicated series of quadratic surfaces is a series (3, 6, 3).

Indeed, we also obtain a series with eight common points and eight common tangential planes possessing the same characteristic numbers (3, 6, 3) when starting from a common polar tetrahedron, a point and a tangential plane *not* passing through this point.

7. We have two more points to consider with respect to our original problem. Firstly, we wish to point out how the case in which O^8 breaks up into four quadratic reguli is easily realised; secondly, we must show that all quadruplets of corresponding rays have hyperboloidic position as soon as this is the case with four of those quadruplets.

When the original part of the locus O^8 is a regulus O^8 the pairs of transversals of the quadruplets of corresponding rays are the pairs of generators of this regulus arrayed in a quadratic involution. If such a quadratic involution of pairs of rays is cut by a plane situated arbitrarily a quadratic involution of pairs of points is generated on a conic; this involution is as one knows characterized by the property, that the connecting lines of the points completing each other to a pair pass through the same point. To realize the above-mentioned case of decomposition of the locus O^8 we start from an arbitrary regulus O^8 , whose generators we regard as paired off in involution in a

definite way, and from four arbitrary planes $\alpha_1, \alpha_2, \alpha_3, \alpha_4$. If then the pencils of rays in those planes lying perspectively to the quadratic involutions of points of the sections are taken as the projectively related pencils of rays of the problem, then the surface O^2 is evidently the integrating part of the corresponding surface O^3 , so this must really also be completed to a surface of order eight by three other reguli O^2 . To conform this we allow an analytical treatment to follow this geometrical consideration.

We suppose the locus proper O^2 to be decomposed into its generators by means of the equations

$$\left. \begin{aligned} p + \lambda q &= 0 \\ r + \lambda s &= 0 \end{aligned} \right\}$$

and we assume that the generators belonging to $\lambda = 0$ and to $\lambda = \infty$ represent the double rays of the quadratic involution on O^2 , i.e. that in this involution the rays with the same absolute value of λ correspond to each other. Here p, q, r, s are general linear forms in x, y, z , according to the formula

$$u = u_1x + u_2y + u_3z + u_4, \quad (u = p, q, r, s),$$

whilst the three planes of coordinates $x = 0, y = 0, z = 0$ and the plane at infinity will do duty for the planes $\alpha_1, \alpha_2, \alpha_3, \alpha_4$ of the pencils of rays to be found. The tracing of these pencils is simplified by representing the minors of the determinant

$$\Delta = \begin{vmatrix} p_1 & p_2 & p_3 & p_4 \\ q_1 & q_2 & q_3 & q_4 \\ r_1 & r_2 & r_3 & r_4 \\ s_1 & s_2 & s_3 & s_4 \end{vmatrix}$$

according to the elements p_i, q_i, r_i, s_i by P_i, Q_i, R_i, S_i .

If we perform the described calculation with respect to the plane $x = 0$, there is occasion to represent the equations

$$\left. \begin{aligned} (p_2 + \lambda q_2)y + (p_3 + \lambda q_3)z + p_4 + \lambda q_4 &= 0 \\ (r_2 + \lambda s_2)y + (r_3 + \lambda s_3)z + r_4 + \lambda s_4 &= 0 \end{aligned} \right\},$$

determining together the point belonging to λ of the conic of the section, for shortness'sake by

$$\left. \begin{aligned} (p + \lambda q)_1 &= 0 \\ (r + \lambda s)_1 &= 0 \end{aligned} \right\}.$$

Then

$$(p + \lambda q)_1 + \mu (r + \lambda s)_1 = 0 \quad . \quad . \quad . \quad . \quad . \quad (1)$$

is an arbitrary line through point λ and

$$\begin{vmatrix} p_1 + \lambda q_1 + \mu(r_1 + \lambda s_1) & p_2 + \lambda q_2 + \mu(r_2 + \lambda s_2) & p_3 + \lambda q_3 + \mu(r_3 + \lambda s_3) & p_4 + \lambda q_4 + \mu(r_4 + \lambda s_4) \\ p_1 - \lambda q_1 & p_2 - \lambda q_2 & p_3 - \lambda q_3 & p_4 - \lambda q_4 \\ r_1 - \lambda s_1 & r_2 - \lambda s_2 & r_3 - \lambda s_3 & r_4 - \lambda s_4 \end{vmatrix} = 0$$

is the condition expressing that this line (1) through point λ contains at the same time the point $-\lambda$ and is thus the ray of the pencil looked for, corresponding to the parameter value λ . If for shortness' sake we write here

$$\begin{vmatrix} p_i + \lambda q_i + \mu(r_i + \lambda s_i) \\ p_i - \lambda q_i \\ r_i - \lambda s_i \end{vmatrix} = 0,$$

direct calculation affords

$$\begin{vmatrix} p_i + \lambda q_i \\ p_i - \lambda q_i \\ r_i - \lambda s_i \end{vmatrix} - \mu \begin{vmatrix} r_i + \lambda s_i \\ r_i - \lambda s_i \\ p_i - \lambda q_i \end{vmatrix} = 0,$$

or

$$\begin{vmatrix} p_i \\ q_i \\ r_i - \lambda s_i \end{vmatrix} - \mu \begin{vmatrix} r_i \\ s_i \\ p_i - \lambda q_i \end{vmatrix} = 0,$$

or

$$\begin{vmatrix} p_i \\ q_i \\ r_i \end{vmatrix} - \lambda \begin{vmatrix} p_i \\ q_i \\ s_i \end{vmatrix} - \mu \begin{vmatrix} r_i \\ s_i \\ p_i \end{vmatrix} + \lambda \mu \begin{vmatrix} r_i \\ s_i \\ q_i \end{vmatrix} = 0,$$

i. e.

$$\mu = \frac{S_1 + \lambda R_1}{Q_1 + \lambda P_1};$$

so the equation of the ray under consideration is

$$(Q_1 + \lambda P_1)(p + \lambda q)_1 + (S_1 + \lambda R_1)(r + \lambda s)_1 = 0,$$

which is reducible to

$$(Q_1 p + S_1 r)_1 + \lambda^2 (P_1 q + R_1 s)_1 = 0,$$

as the coefficient of the first power of λ identically vanishes.

If now, for $u = p, q, r, s$, we understand by u_x, u_y, u_z, u_0 the forms into which $u_x x + u_y y + u_z z + u_0$ passes by omitting successively the term with x , the term with y , the term with z or the constant term and if k is substituted for λ^2 the four projectively related pencils are represented in their planes by the equations

$$\left. \begin{aligned} I \dots Q_1 p_x + S_1 r_x + k(P_1 q_x + R_1 s_x) &= 0 \\ II \dots Q_2 p_y + S_2 r_y + k(P_2 q_y + R_2 s_y) &= 0 \\ III \dots Q_3 p_z + S_3 r_z + k(P_3 q_z + R_3 s_z) &= 0 \\ IV \dots Q_4 p_o + S_4 r_o + k(P_4 q_o + R_4 s_o) &= 0 \end{aligned} \right\} \dots (2)$$

For which values of k have these four rays hyperboloidic position? To this end it is necessary and sufficient that the points at infinity of I, II, III lie on a right line. So for k we find the cubic equation:

$$\begin{vmatrix} 0 & Q_1 p_o + S_1 r_o + k(P_1 q_o + R_1 s_o) & -[Q_1 p_x + S_1 r_x + k(P_1 q_x + R_1 s_x)] \\ -[Q_2 p_x + S_2 r_x + k(P_2 q_x + R_2 s_x)] & 0 & Q_2 p_o + S_2 r_o + k(P_2 q_o + R_2 s_o) \\ Q_3 p_x + S_3 r_x + k(P_3 q_x + R_3 s_x) & -[Q_3 p_o + S_3 r_o + k(P_3 q_o + R_3 s_o)] & 0 \end{vmatrix} = 0$$

So in reality three reguli have separated from the surface O^3 .

8. Finally we have still to indicate that all quadruplets of corresponding rays lie hyperboloidically if four quadruplets do. This proof we join on to the most general case of four arbitrary planes $\alpha_1, \alpha_2, \alpha_3, \alpha_4$ and four arbitrary points O_1, O_2, O_3, O_4 in them. If A_1, A_2, A_3, A_4 is the face α_1 no longer equilateral, then the projective pencils $(l_1), (l_2), (l_3), (l_4)$ describe on the sides $A_1 A_2, A_2 A_3, A_3 A_4, A_4 A_1$ the projective series of points $(C_1), (D_1), (B_1)$ possessing for $k=4$ four triplets of points on the same right line. In that case the conics enveloped by the connecting lines $C_1 D_1$ and $D_1 B_1$ have five common tangents, i.e. $A_1 A_2$ and the four lines bearing corresponding triplets of points; then those conics coincide. So the supposition of four such triplets leads to the case that there is an infinite number of such triplets. But then in each of the four planes $\alpha_1, \alpha_2, \alpha_3, \alpha_4$ lies a common transversal of each corresponding quadruplet, etc.

We now conclude by showing that in order to determine four projectively related pencils of rays with merely hyperboloidic quadruplets the four planes $\alpha_1, \alpha_2, \alpha_3, \alpha_4$ and the four vertices O_1, O_2, O_3, O_4 in them can be taken arbitrarily by showing that to a ray l_1 drawn arbitrarily in α_1 through O_1 only a single triplet of rays l_2, l_3, l_4 of the remaining pencils corresponds, forming with l_1 four lines with hyperboloidic position crossing each other.

If μ, v, ϱ represent successively the conditions that a quadratic surface contains a point, touches a line and touches a plane, then

$$\frac{1}{4} V_6 \{2v^3 - 3v^2(\mu + \varrho) + v(3\mu^2 + 2\mu\varrho + 3\varrho^2) - 2(\mu^3 + \varrho^3)\}$$

indicates according to HURWITZ the number of surfaces through an arbitrary line, which satisfy the sixfold condition V_6 (*Math. Ann.*, vol. 10, page 354). So the number of quadratic surfaces through l_1

containing the points O_1, O_2, O_3 and touching the planes $\alpha_1, \alpha_2, \alpha_3$ is represented by

$$\frac{1}{4} \mu^2 \varphi^2 \{2v^2 - 3v^2 (\mu + \varphi) + v (3\mu^2 + 2\mu\varphi + 3\varphi^2) - 2(\mu^2 + \varphi^2)\},$$

which in connection with the law of duality can be deduced to

$$\frac{1}{2} \mu^2 \varphi^2 \{v^2 - 3\mu v^2 + 3\mu^2 v + \mu v \varphi - 2\mu^2\}.$$

Out of the wellknown results (H. SCHUBERT, "Kalkül der abzählenden Geometrie", Leipzig, Teubner, 1879)

$\mu^2 v^2 \varphi^2 = 104$, $\mu^2 v^2 \varphi^2 = 68$, $\mu^2 v \varphi^2 = 42$, $\mu^2 v \varphi^2 = 34$, $\mu^2 \varphi^2 = 17$
we find that there are five quadratic surfaces satisfying the given conditions.

However it is now easy to see, that only one of those five solutions furnishes four hyperboloidic lines l_1, l_2, l_3, l_4 crossing each other. We find namely four solutions not to be used for our purpose (fig. 5) if we determine l_1, l_2, l_3, l_4 in such a way so as to cut the given

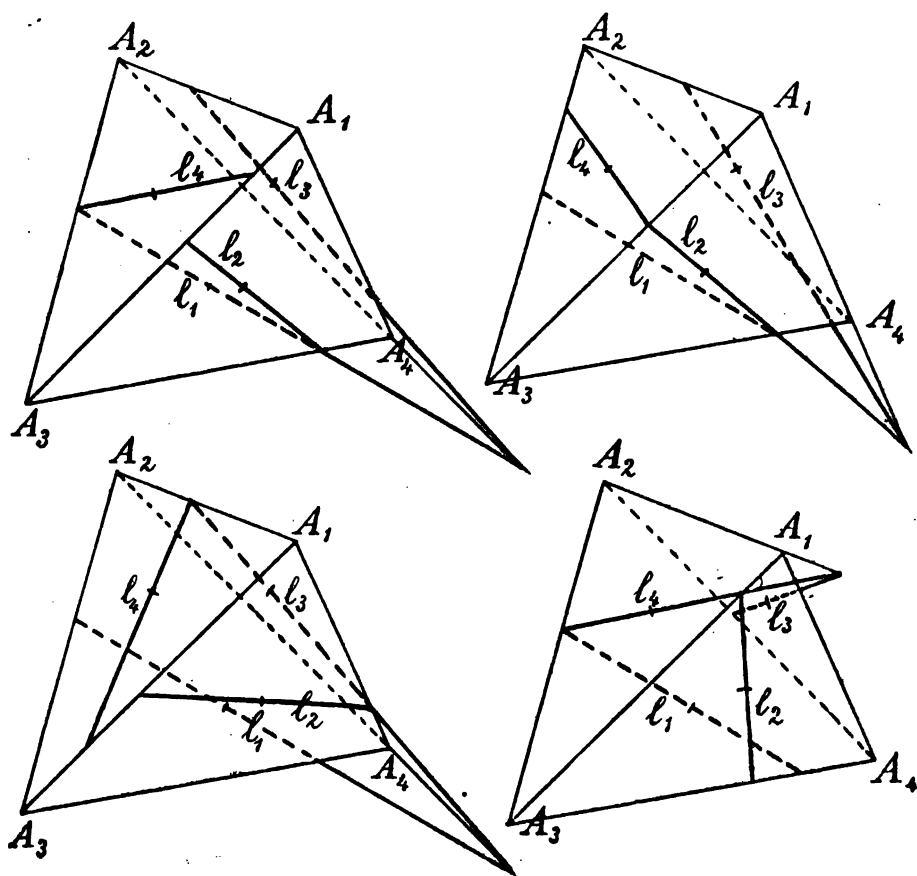


Fig. 5.

line l_1 , or when having taken one of these three lines in that manner we choose the other two in such a way that they both cut this new line. So there is only one solution, in which the four lines l_1, l_2, l_3, l_4 cross each other.

From the above consideration which can easily be confirmed analytically ensues that the supposition of four planes α_i given arbitrarily and of four vertices O_i given arbitrarily dominates the case of four projective pencils of rays with merely hyperboloidic quadruplets to such an extent that the projective correspondence is fixed by the condition of the hyperboloidic position. This now again includes that the case of the three quadruplets with hyperboloidic position, treated above in details, cannot present itself if the planes α_i and the points O_i have been taken arbitrarily. For these three quadruplets must also put in an appearance if we wish all quadruplets to have hyperboloidic position, and they determine the projective relation unequivocally, i.e. three hyperboloidic quadruplets lead here to pure hyperboloidic quadruplets.

Not to get too redundant, we put aside the examination of the less remarkable series of quadratic surfaces, answering to this most general case of four pencils of rays with merely hyperboloidic quadruplets.

Astronomy. — "*On the orbital planes of Jupiter's satellites*". By Dr. W. DE SITTER. (Communicated by Prof. J. C. KAPTEYN).

The following pages contain a condensed summary of the results of an investigation, which will soon be published in detail in the "*Annals of the Royal Observatory at the Cape of Good Hope*". The material on which this investigation is based consists entirely of observations made at the Cape Observatory, viz.:

1. Heliometer-observations made in 1891 by GILL and FINLAY, discussed by me and published in my inaugural dissertation.¹⁾
2. Photographic plates taken at the Cape Observatory in 1891, measured and discussed by me.
3. Heliometer-observations made in 1901 and 1902 by COOKSON, discussed by himself and published in *Monthly Notices*, June 1904 p. 728—747.
4. Photographic plates taken in 1903 and 1904, measured and discussed by me.

¹⁾ Discussion of Heliometer-Observations of Jupiter's Satellites, Groningen J. B. WOLTERS 1901.

My aim with this investigation was exclusively the determination of the inclinations and nodes of the orbital planes of the satellites and of the motions of these nodes. The plates of 1903 and 1904 were taken in order to provide a second epoch from which these motions could be determined by a comparison with the observations of 1891.

The fine series of observations, made by Mr. BRYAN COOKSON in 1901 and 1902 increases the weight of this determination considerably.

I have already pointed out, in the fourth chapter of my dissertation, that the determination of the other elements, which must be derived from the observed (jovicentric) longitudes, is probably sufficiently provided for by the observations of eclipses. Moreover from the observations mentioned above sub 1. and 3. *all* elements were determined.

Eclipse-observations are however not well adapted for the determination of the inclinations and nodes, which must be derived from the observed latitudes, as I have shown, l. c. page 77. The principal interest of the determination of the orbital planes lies in the comparison with the observations of the large motions of the nodes, which are demanded by the theory. Since these motions are produced almost exclusively by the large polar compression of the planet, the natural fundamental plane to which the latitudes must be referred is the equator of Jupiter.

If we refer the positions of the satellites to a system of co-ordinate axes, of which the axis of y is the projection on the sphere of a line perpendicular to this fundamental plane (i. e. of Jupiter's axis of rotation), and the axis of x is the great circle through the centre of the planet perpendicular to the axis of y , then for the determination of the inclinations and nodes the y co-ordinates of the satellites are alone important. Only these co-ordinates have therefore been measured. The plate was, by means of the position-circle with which the Repsold measuring machine of the Astronomical Laboratory at Groningen is provided, brought approximately in the position-angle $P + 90^\circ$, where P is the position-angle of Jupiter's adopted axis of rotation. The plate then has a motion parallel to a straight line, which nearly coincides with the axis of x , and which is defined by the axis of the cylinder which guides the plate-holder in its motion. The co-ordinates perpendicular to this straight line were then measured by the micrometer screw. These differ from the co-ordinates y only by small corrections (refraction, orientation and scale-value). In this method the measured quantities never exceed a few revolutions of the screw. All errors of réseau-lines, division errors of the scales,

error of projection, etc. are avoided. The straightness of the cylinder was repeatedly tested by comparison with a stretched spiderline. Its errors are certainly smaller than 0.2 micron. The position-angles were read off by two microscopes, and the orientation of the plate was determined from a pair of standard stars, which were for this purpose photographed on each plate, and from trails of the satellites. The errors of observation of the measures of the satellites are satisfactory, distortion of the photographic film cannot be detected, and the discussion of a dozen plates, which were specially taken for this purpose, shows that the determination of the orientation from the trails is always practically free from systematic errors, while the same can be said of the determination from the standard stars under certain conditions, which are however not always fulfilled. The accidental errors of both determinations are very small.

The image of the planet has not been measured. The observed co-ordinates contain therefore an unknown additive constant (different for each separate plate), which was eliminated by using in the subsequent reductions the co-ordinates referred to the mean of all the satellites occurring on the plate as origin. The equations of condition and normal equations for these relative co-ordinates are very simple and symmetrical. The limited space at my disposal prevents me however from entering into more details regarding the measures and reductions. I will at once state the results.

The unknowns which were determined from each opposition were the corrections to the adopted values of the elements p and q of the four satellites which are defined by the formulas:

$$p = i \sin(-\Omega)$$

$$q = i \cos(-\Omega)$$

where i and Ω are the inclination and ascending node of the orbital plane of the satellite referred to the fundamental plane. The longitude of the node is counted from the ascending node of the plane of Jupiter's orbit on the fundamental plane. The quantities referring to the four satellites are distinguished by the suffixed numerals 1 to 4.

The following table contains the results of the different series of observations with their probable errors.

The values for 1891 (*Helimeter*) are those derived in my dissertation with a few insignificant corrections in the last decimal places. The results from the heliometer and those from the plates have been combined with the relative weights 2 and 1.

The results for 1901 and 1902 are quoted from the communication by Mr. Cookson in the Monthly Notices.

I have however been compelled to reject Δp_1 and Δq_1 for 1901

	1891.75 Heliumeter.	1891.75 Plates.	1891.75
Δp_1	$+ 0.0409 \pm .0052$	$+ 0.0372 \pm .0050$	$+ 0.0397 \pm .0038$
Δp_2	$+ .0740 \pm 36$	$+ .0733 \pm 36$	$+ .0738 \pm 27$
Δp_3	$- .0033 \pm 23$	$- .0024 \pm 19$	$- .0030 \pm 17$
Δp_4	$+ .0642 \pm 12$	$+ .0638 \pm 12$	$+ .0641 \pm 9$
Δq_1	$- 0.0259 \pm .0056$	$- 0.0258 \pm .0061$	$- 0.0259 \pm .0043$
Δq_2	$+ .0853 \pm 33$	$+ .0813 \pm 35$	$+ .0840 \pm 25$
Δq_3	$- .0683 \pm 20$	$- .0748 \pm 23$	$- .0705 \pm 16$
Δq_4	$- .0137 \pm 12$	$- .0117 \pm 11$	$- .0130 \pm 9$

	1901.61 COOKSON.	1902.62 COOKSON.	1903.72 Plates.	1904.89 Plates.
Δp_1	$+ 0.0170 \pm .0077$	$+ 0.0137 \pm .0072$	$+ 0.0021 \pm .0060$	$- 0.0028 \pm .0078$
Δp_2	$+ .1113 \pm 56$	$+ .0922 \pm 44$	$+ .0526 \pm 33$	$+ .0158 \pm 44$
Δp_3	$- .0148 \pm 36$	$- .0072 \pm 28$	$- .0199 \pm 22$	$- .0104 \pm 28$
Δp_4	$+ .0456 \pm 18$	$+ .0658 \pm 15$	$+ .0637 \pm 12$	$+ .0648 \pm 13$
Δq_1	$- 0.0695 \pm .0084$	$- 0.0755 \pm .0065$	$- 0.0597 \pm .0048$	$- 0.0335 \pm .0077$
Δq_2	$- .1770 \pm 49$	$- .1860 \pm 40$	$- .2120 \pm 32$	$- .2252 \pm 48$
Δq_3	$- .0360 \pm 33$	$- .0334 \pm 23$	$- .0494 \pm 20$	$- .0476 \pm 26$
Δq_4	$- .0359 \pm 18$	$- .0070 \pm 14$	$- .0284 \pm 11$	$- .0209 \pm 17$

and 1902. COOKSON found from the reduction of his observations that the residuals could be much reduced by assuming in the latitude of satellite IV an inequality of which the period is one half of the periodic time of the satellite while the coefficient is about $50''$. I have searched for this inequality in the observations of 1891, 1903 and 1904 and I can confidently declare that in none of these years there is even the slightest trace of any inequality of which the argument should be a multiple of the mean longitude of Sat. IV. Since also an inequality of this nature cannot be explained by the theory I cannot but doubt its reality, and since the cause which has produced this apparent inequality must necessarily also have affected the determination of p_4 and q_4 , the safest course seemed to be to reject the values of these elements found from the observations of 1901

and 1902. All other corrections Δp and Δq derived from the observations are included in the following discussion, with weights inversely proportional to the squares of their probable errors and corresponding to a p. e. of weight unity of ± 0.0050 .

Before this discussion can be related the theoretical expressions for p and q must be developed.

At the time when the analytical theory of the satellites was created by LAGRANGE and LAPLACE, the eclipses were practically the only phenomena of the satellites which were observed. For these the natural fundamental plane is the plane containing the axis of the shadow-cone, i. e. the plane of Jupiter's orbit. This was accordingly used by them. SOUILLART, in his theory published in 1880, followed their example.

The first thing which must be done before the theory can be compared with modern observations is thus to reduce the expressions for the latitudes referred to Jupiter's orbit to latitudes referred to the equator. This has already been done by MARTH, who in 1891 published tables for the computation of the co-ordinates of the satellites, based on SOUILLART's theory (Monthly Notices, June 1891, pages 505—539).

Let I and N be the inclination and node¹⁾ of the orbital plane of one of the satellites with reference to the orbit of Jupiter. SOUILLART's theory then gives

$$\left. \begin{aligned} I_i \sin N_i &= \sum_{j=1}^4 b_{ij} \sin \theta_j + \mu_i \omega \sin \theta_0 \\ I_i \cos N_i &= \sum_{j=1}^4 b_{ij} \cos \theta_j + \mu_i \omega \cos \theta_0 \end{aligned} \right\} \dots \dots (1)$$

In these formulae ω and θ_0 are the inclination and node of Jupiter's equator on its orbit. All longitudes are counted from the first point of Aries. The quantities b_{ij} are constants, and the angles θ_i vary proportionally with the time. Of the constants b_{ij} four only are mutually independent. If we put:

$$b_{ii} = \gamma_i \quad b_{ij} = \sigma_{ij} \gamma_j,$$

then the γ_i are constants. The multipliers σ_{ij} and μ_i and the coefficients of the time in the expressions for θ_i are given by the theory as functions of the masses, the compression of Jupiter and the mean motions. The constants σ_{ij} are small numbers (the largest is $\sigma_{43} = 0.1944$) with the exception, of course, of those in the diagonal, $\sigma_{ii} = 1$. The value of μ_i differs little from unity. The angles γ_i and θ_i are what LAPLACE calls the "inclinaisons et noeuds propres" of the satellites.

¹⁾ With node I mean ascending node, unless otherwise stated.

Let now ω_0 and ψ_0 be the inclination and the longitude (counted from the first point of Aries) of the descending node of the plane which I wish to adopt as the fundamental plane, referred to the plane of Jupiter's orbit. Longitudes in the fundamental plane are counted from the node ψ_0 as zero.

Then if i and δ_0 are the inclination and node of the orbit of one of the satellites referred to the fundamental plane, we have, neglecting quantities of the third order in i , I and ω_0 :

$$\begin{aligned} i \sin \delta_0 &= I \sin (N - \psi_0) \\ i \cos \delta_0 &= I \cos (N - \psi_0) + \omega_0 \end{aligned}$$

If further we introduce the notations

$$\left. \begin{aligned} \Gamma_i &= \psi_0 - \theta_i & \psi &= \psi_0 - \theta_0 + 180^\circ \\ x_i &= \gamma_i \sin \Gamma_i & x_0 &= \omega \sin \psi \\ y_i &= \gamma_i \cos \Gamma_i & y_0 &= \omega \cos \psi - \omega_0 \end{aligned} \right\} \dots \dots (2)$$

then the expressions for p and q become:

$$\left. \begin{aligned} p_i &= \sum_{j=1}^4 \sigma_{ij} x_j - \mu_i x_0 \\ q_i &= \sum_{j=1}^4 \sigma_{ij} y_j + (1 - \mu_i) \omega_0 - \mu_i y_0 \end{aligned} \right\} \dots \dots (3)$$

MARTH has adopted

$$\left. \begin{aligned} \omega_0 &= \text{the value of } \omega \\ \psi_0 &= \text{,, ,, ,, } \theta_0 + 180^\circ \end{aligned} \right\} \text{ from SOUILLART's theory, } ^1)$$

and has computed the values of p and q by the formulae (3), taking $x_0 = y_0 = 0$.

The unknowns γ_i , Γ_i , x_0 and y_0 must be determined from the equations (3). This is, of course, only possible if the coefficients σ_{ij} and μ_i are known. I have adopted these coefficients from SOUILLART's theory, as being the best available. They are very complicated functions of the masses, the compression of Jupiter, and the mean motions. As a rough approximation, we can say that the coefficients σ_{ij} are proportional to the mass m_j . Since the masses are very imperfectly known, the same thing is true of the coefficients of the equations (3). Therefore the results of the present discussion cannot be considered as final, but the discussion will have to be repeated when better values of the coefficients are available. The results here derived will however doubtlessly represent a very fair approximation.

It may perhaps be mentioned that the uncertainty of these coeffi-

¹⁾ MARTH has made one or two mistakes here, which will be duly mentioned in the detailed publication, but as they have no influence on the result they can be ignored at present.

icients is not due to our ignorance with respect to the masses alone. The values of these coefficients derived by SOUILLART from *the same* masses and elements by two different methods of integration show differences of such amount, that the consequent differences in the computed values of p and q are of the order of the errors of observation. It is hardly to be expected that this defect in the theory will be remedied before the equator is introduced instead of the orbit as the fundamental plane of the theory. The coefficients adopted by MARTH and myself are those derived from the second method of integration, which is also preferred by SOUILLART himself.

In the following discussions these coefficients are treated as absolute constants. If we denote the corrections to the adopted values of x_i and y_i by δx_i and δy_i , then the unknowns

$$\delta x_i \quad \delta y_i \quad x_0 \quad y_0$$

must be determined from the equations

$$\left. \begin{aligned} \sum \sigma_{ij} \delta x_j - \mu_i x_0 &= \Delta p_i \\ \sum \sigma_{ij} \delta y_j - \mu_i y_0 &= \Delta q_i \end{aligned} \right\} \dots \dots \dots (4)$$

The term $(1 - \mu_i) \omega_0$ in the second equation (3) must, of course, be treated as rigorously known.

The solution of the equations (4) is conducted in the following manner. I define the quantities Δx_i and Δy_i by the equations

$$\left. \begin{aligned} \sum \sigma_{ij} \Delta x_j &= \Delta p_i \\ \sum \sigma_{ij} \Delta y_j &= \Delta q_i \end{aligned} \right\} \dots \dots \dots (5)$$

These equations are solved once and for all, and the solution is:

$$\left. \begin{aligned} \Delta x_i &= \sum \sigma_{ij}' \Delta p_j \\ \Delta y_i &= \sum \sigma_{ij}' \Delta q_j \end{aligned} \right\} \dots \dots \dots (6)$$

Further, if we put:

$$\mu_i' = \sum \sigma_{ij}' \mu_j$$

then the equations of condition become:

$$\left. \begin{aligned} \delta x_i - \mu_i' x_0 &= \Delta x_i \\ \delta y_i - \mu_i' y_0 &= \Delta y_i \end{aligned} \right\} \dots \dots \dots (7)$$

Next, if we denote the originally adopted values of x_i and y_i by x_{i_0} and y_{i_0} so that $x_i = x_{i_0} + \delta x_i$, $y_i = y_{i_0} + \delta y_i$, then the equations become:

$$\left. \begin{aligned} x_i - \mu_i' x_0 &= x_{i_0} + \Delta x_i \\ y_i - \mu_i' y_0 &= y_{i_0} + \Delta y_i \end{aligned} \right\} \dots \dots \dots (8)$$

In these equations x_i and y_i are defined by the equations (2), where the γ_i are constants, and $\Gamma_i = \Gamma_{i_0} + \frac{d\Gamma_i}{dt} (t - t_0)$. The unknowns, which

must be determined from the solution of the equations (8) are $x_0, y_0, \gamma_i, \Gamma_i$, and $\frac{d\Gamma_i}{dt}$.

The values of $\frac{d\Gamma_i}{dt}$ for the four satellites are however not mutually independent. The theory gives these differential coefficients as functions of the masses of the satellites and the compression of Jupiter. The masses need not be considered here. I have tried to determine a correction to m_0 , but this determination had too small a weight to have any real value. The influence of the other masses is even smaller.

The compression enters into the formulas through the factor Jb^2 , where J is the well known constant, which is approximately equal to $\varphi - \frac{1}{2}\varphi$ (φ = ellipticity of the free surface, φ = ratio of centrifugal force to gravity at the equator of Jupiter) and b is the equatorial radius¹⁾ of the planet.

If we introduce as unknown:

$$x = \frac{\delta J b^2}{J b^2}$$

then the true values of the coefficients of t are

$$\frac{d\Gamma_i}{dt} = \left(\frac{d\Gamma_i}{dt} \right)_0 + a_i x$$

The coefficients a_i depend practically alone on the mean motions, and must be treated as absolute constants. They differ little from $\frac{d\Gamma_i}{dt}$ itself, and consequently the *ratios* of the motions of the nodes must be considered as approximately constant. The adopted values according to SOUILLART's theory are (daily motions):

$$\begin{aligned} \left(\frac{d\Gamma_1}{dt} \right)_0 &= 0^\circ.14109 & \left(\frac{d\Gamma_2}{dt} \right)_0 &= 0^\circ.007019 \\ \left(\frac{d\Gamma_3}{dt} \right)_0 &= 0^\circ.033010 & \left(\frac{d\Gamma_4}{dt} \right)_0 &= 0^\circ.001898 \end{aligned}$$

The 36 equations (8) thus contain the 11 unknowns

$$\gamma_i \quad \Gamma_i \quad x_0 \quad y_0 \quad x$$

These equations must be solved by successive approximations. The conditions for the application of the method of least squares are far from being fulfilled.

These approximations have been conducted in the following manner.

¹⁾ In the original Dutch b was erroneously stated to be the diameter, instead of the radius.

Let x_{00} , y_{00} be approximate values of x_0 and y_0 , thus $x_0 = x_{00} + \delta x_0$ and $y_0 = y_{00} + \delta y_0$. We have then:

$$\left. \begin{aligned} x_i - \mu_i' \delta x_0 &= x_{i0} + \Delta x_i + \mu_i' x_{00} \\ y_i - \mu_i' \delta y_0 &= y_{i0} + \Delta y_i + \mu_i' y_{00} \end{aligned} \right\} \dots \dots \dots (9)$$

If we suppose that the approximation x_{00} , y_{00} is already so good that δx_0 and δy_0 can be neglected, then these equations become:

$$\left. \begin{aligned} \gamma_i \sin \Gamma_i &= x_{i0} + \Delta x_i + \mu_i' x_{00} \\ \gamma_i \cos \Gamma_i &= y_{i0} + \Delta y_i + \mu_i' y_{00} \end{aligned} \right\} \dots \dots \dots (10)$$

Next I compute the quantities g_i and G_i from the equations:

$$\left. \begin{aligned} g_i \sin G_i &= x_{i0} + \Delta x_i + \mu_i' x_{00} \\ g_i \cos G_i &= y_{i0} + \Delta y_i + \mu_i' y_{00} \end{aligned} \right\} \dots \dots \dots (11)$$

The other unknowns are then determined from the equations:

$$\left. \begin{aligned} \gamma_i &= g_i \\ \Gamma_i + \frac{d\Gamma_i}{dt}(t-t_0) &= G_i \end{aligned} \right\} \dots \dots \dots (12)$$

If these equations give constant values for γ_i and values of $\frac{d\Gamma_i}{dt}$, which can by an acceptable value of κ be made consistent with the theory, then the approximation is sufficient, if not, then a new approximation must be made. As a first approximation I have assumed:

$$x_{00} = y_{00} = 0.$$

The equations (12) were then formed and solved. In this solution I have determined the values of $\frac{d\Gamma_i}{dt}$ for the four satellites separately without introducing the theoretical ratios ab initio. The equations (12) then consist of two sets for each satellite and each of these 8 sets is independent of all others. The residuals which remain after the substitution of the resulting values of the unknowns will be given below together with those from the other solutions. The probable error of unit weight was $\pm 0^{\circ}.0086$.

The motions of the nodes in this solution are (Sol. I):

$$\begin{aligned} \frac{d\Gamma_1}{dt} &= 0^{\circ}.01213 & \frac{d\Gamma_2}{dt} &= 0^{\circ}.00587 \\ \frac{d\Gamma_3}{dt} &= 0^{\circ}.080266 & \frac{d\Gamma_4}{dt} &= 0^{\circ}.00189. \end{aligned}$$

If these are compared with the theoretical values, it appears at once that their ratios are very different. The node of satellite I, which according to the theory has a yearly motion of about 50° , in this solution shows a motion of about 5° . The ratios of the three

other motions also differ considerably from their theoretical values. Moreover the inclinations are far from constant, as will be seen at once from an inspection of the residuals $\Delta\gamma$.

It must be mentioned that the value of $\frac{d\Gamma_2}{dt}$ agrees approximately with the value derived by COOKSON from the observations of 1891, 1901 and 1902. This could have been expected since COOKSON in this determination also neglected the corrections to the position of the equator. The difference between COOKSON's value of $\frac{d\Gamma_2}{dt}$ and the value of Sol. I is not due to a bad agreement of the observations of 1903 and 1904 with those of 1901 and 1902 (which on the contrary agree extremely well), but to the fact that in Sol. I the corrections to the elements of the other satellites were eliminated by means of the transformation from Δp and Δq to Δx and Δy , while COOKSON did not eliminate these corrections but neglected them.

I have now made a number of further solutions, in which I started with approximate values x_0 , and y_0 , and introduced the unknowns

$$\gamma, \quad \Gamma_0, \quad \delta x, \quad \delta y, \quad x,$$

thus rigorously subjecting the motions of the nodes to the theoretical condition. The unknowns δy , and x are badly separated. The weight of the determination of x is considerably diminished by the introduction as unknowns of the corrections to the position of the equator. That this must of necessity be so, is easily seen. If we had observations of only one satellite at two epochs, it would be impossible to determine both the motion of the node and the equator. We would in that case have only four data (the values of p and q at each of the epochs) for the determination of the five unknowns γ , Γ , $\frac{d\Gamma}{dt}$, x_0 , and y_0 . Now x is practically determined from satellite II alone. The motions of the nodes of III and IV are too slow, and the inclination of I is too small, to allow a determination of the motions of the nodes of these satellites to be made, the accuracy of which would be even remotely comparable to that of sat. II. The motions of the nodes of I, III and IV are derived theoretically from that of II. If therefore the latter is known, each of the three others provides a determination of the equator. Then the determination of x from II must be repeated with this new position of the equator, and so on until a satisfactory agreement is reached.¹⁾

¹⁾ COOKSON has in his discussion of the observations of 1891, 1901 and 1902, used this method, but he rested content with the first approximation. His corrections to the equator derived from satellites III and IV are in the same direction as the values found by me.

The solution was not actually made in this way, but all equations were treated simultaneously. This consideration is only given here to point out that the position of the equator is ultimately determined by the condition that it shall be the same for the four satellites, i. e. that the inclinations shall be constant, and the motions of the nodes shall be consistent with the theoretical ratios. Since a small displacement of the equator has a large influence on the motions of the nodes, in consequence of the small inclinations, it can be expected that the unknown κ and the quantities which determine the position of the equator will mutually diminish each others weights. (That this decrease of weight is actually much more marked in the case of y_0 than for x_0 , is accidental and depends on the choice of the zero of longitudes).

By these considerations I have been led to try whether the value of κ could not be determined from a comparison with other observations. I have used the values of θ_i for 1750 given by DELAMBRE. A value of κ was adopted, such that the value of θ_i carried back to 1750 from the modern observations would be nearly equal to the value given by DELAMBRE. The unknowns x_0 , y_0 , $\sigma\gamma_i$ and σF_i were then determined from the modern observations alone.

This gives solution VII. In solution VI on the other hand all unknowns (inclusive of κ) were determined from the modern observations. I give below the results from these two solutions, which I consider as the best that can be derived with our present knowledge of the masses. I do not venture to choose between the two solutions. Probably an eventual correction of the coefficients $\sigma\gamma_i$ will tend to reconcile the two solutions.

Instead of F_i I give at once $\theta_i = \psi_0 - F_i$. The values are given for 1900 Jan. 0 Greenwich Mean Noon.

	<i>Solution VI</i>	<i>Solution VII</i>	<i>Adopted values.</i>
x_0 —	$0^\circ.0172 \pm .0023$	$-0^\circ.0177 \pm .0022$	0
y_0 +	$0.0427 \pm .0048$	$+0.0489 \pm .0022$	0
κ —	$0.0321 \pm .0094$	-0.0126	0
γ_1	$0^\circ.0259 \pm .0032$	$0^\circ.0248 \pm .0038$	$0^\circ.0013$
γ_2	$.4696 \pm 27$	$.4676 \pm 24$	$.4694$
γ_3	$.1926 \pm 40$	$.1874 \pm 26$	$.1789$
γ_4	$.2540 \pm 34$	$.2504 \pm 25$	$.2254$
θ_1	$54^\circ.4 \pm 8^\circ.5$	$54^\circ.0 \pm 8^\circ.8$	$99^\circ.8$
θ_2	293.42 ± 0.85	293.10 ± 0.29	273.32
θ_3	319.68 ± 0.77	319.67 ± 0.80	330.59
θ_4	14.40 ± 0.91	15.56 ± 0.57	5.79

From the values of κ we find the following values of $\frac{d\theta}{dt}$

$\frac{d\theta_1}{dt}$	— 0°.13664	— 0°.13932	— 0°.14105
$\frac{d\theta_2}{dt}$	— 0.032105	— 0.032633	— 0.032974
$\frac{d\theta_3}{dt}$	— 0.006814	— 0.006916	— 0.006983
$\frac{d\theta_4}{dt}$	— 0.001839	— 0.001854	— 0.001863

From the values of x , and y , we find for the inclination and node of the equator on LEVERRIER'S orbit of Jupiter of 1900.0 :

ω	3°.1107 \pm °.0043	3°.1169 \pm °.0022	3°.0680
θ	315.727 \pm .042	315.735 \pm .041	315.410

With the exception of κ all unknowns in the two solutions agree within the sum of their probable errors, and with only one exception (γ_2) all the corrections to the adopted values are many times larger than their probable errors.

The residuals of the two solutions VI and VII are given in the following table together with those of Sol. I. The probable errors, which have been added for comparison are somewhat larger than those of the observed Δp and Δq , because by the transformation from Δp and Δq to Δx and Δy , the p.e. must be somewhat increased, even if we consider the coefficients σ_{ij} as absolutely exact.

The p.e. of weight unity, which was $\pm 0''.0086$ for Sol. I, is $\pm 0''.0065$ for Sol. VI and $\pm 0''.0064$ for Sol. VII. But it is chiefly in their consistency with the theoretical conditions, that both solutions are incomparably better than Sol. I. The inclinations are now constant within the probable errors. The residuals of the nodes only show a systematic tendency for Satellite I (in Sol. VII, where the motions of the nodes were not derived from the observations, also for Sat. II). Still the agreement with the theoretical motions is much improved.

The value of $\frac{d\Gamma_1}{dt}$ derived from Sol. VI irrespective of the theoretical conditions would be 0°.1250, while the value corresponding to the value of κ in this solution is 0°.1366. This is a great improvement compared with Sol. I (0°.0121).

The results for Sat. III in 1901 and 1902, which in all solutions gave large residuals, have in the solutions VI and VII been rejected. This rejection has no appreciable influence on the values of the unknowns, nor on the other residuals, but it reduces the p. e. of

	<i>p. e.</i>	Sol. I		Sol. VI		Sol. VII	
		$\Delta \gamma$	$\sin \gamma \Delta \Gamma$	$\Delta \gamma$	$\sin \gamma \Delta \Gamma$	$\Delta \gamma$	$\sin \gamma \Delta \Gamma$
Sat. I.	1891	$\pm .0045$	$-.0068$ $-.0003$	$+.0005$ $+.0123$	$+.0047$ $+.0093$		
	1901	\pm 85	$+$ 157 $-$ 32	$-$ 12 $+$ 101	$-$ 60 $+$ 99		
	02	\pm 75	$+$ 213 $-$ 38	$+$ 55 $-$ 97	$+$ 8 $-$ 100		
	03	\pm 60	$+$ 37 $+$ 34	$-$ 33 $-$ 155	$-$ 61 $-$ 112		
	04	\pm 80	$-$ 237 $+$ 48	$-$ 5 $-$ 99	$+$ 38 $-$ 78		
Sat. II.	1891	$\pm .0030$	$+.0138$ $+.0002$	$+.0017$ $-.0008$	$+.0016$ $+.0045$		
	1901	\pm 60	$+$ 137 $-$ 40	$+$ 73 $+$ 20	$+$ 56 $+$ 8		
	02	\pm 50	$-$ 73 $+$ 2	$-$ 63 $+$ 50	$-$ 65 $+$ 29		
	03	\pm 40	$-$ 95 $+$ 6	$-$ 2 $+$ 4	$+$ 1 $-$ 29		
	04	\pm 50	$-$ 210 $+$ 8	$-$ 30 $-$ 54	$-$ 13 $-$ 104		
Sat. III.	1891	$\pm .0020$	$+.0048$ $+.0007$	$-$ 0014 $-.0029$	$-.0013$ $-.0037$		
	1901	\pm 40	$-$ 137 $-$ 33	$[-$ 178] $[-$ 29]	$[-$ 181] $[-$ 24]		
	02	\pm 30	$-$ 114 $-$ 77	$[-$ 152] $[-$ 73]	$[-$ 155] $[-$ 67]		
	03	\pm 25	$+$ 32 $+$ 57	$+$ 11 $+$ 56	$+$ 10 $+$ 62		
	04	\pm 30	$+$ 33 $-$ 30	$+$ 14 $-$ 31	$+$ 12 $-$ 22		
Sat. IV.	1891	$\pm .0010$	$-.0010$ $+.0001$	$+.0013$ $-.0028$	$+.0017$ $-.0031$		
	1901	\pm 20	$[-$ 51] $[-$ 188]	$[-$ 101] $[-$ 205]	$[-$ 110] $[-$ 200]		
	02	\pm 20	$[-$ 86] $[-$ 185]	$[-$ 83] $[-$ 166]	$[-$ 85] $[-$ 171]		
	03	\pm 15	$+$ 22 $+$ 28	$-$ 4 $+$ 61	$-$ 7 $+$ 62		
	04	\pm 20	$-$ 11 $-$ 60	$-$ 30 $-$ 20	$-$ 34 $-$ 21		

weight unity from $\pm 0^{\circ}.0072$ and $\pm 0^{\circ}.0073$ to $\pm 0^{\circ}.0065$ and $\pm 0^{\circ}.0064$ for the solutions VI and VII respectively.

The values of θ_i carried back to 1750 are:

	Sol. I	Sol. VI	Sol. VII	Damoiseau	Delambre
θ_1	151°.8	252°.4	281°.0	282°.0	283°.3
θ_2	282°.9	333°.0	338°.6	353°.5	352°.5
θ_3	110°.3	114°.2	117°.1	98°.3	105°.0

In conclusion I must express my deep sense of gratitude towards Sir DAVID GILL, who liberally placed the observations of the Cape Observatory at my disposal, and was always ready to meet all my wishes.

(April 24, 1906).

KONINKLIJKE AKADEMIE VAN WETENSCHAPPEN
TE AMSTERDAM.

PROCEEDINGS OF THE MEETING
of Friday April 27, 1906.

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Afdeeling van Zaterdag 31 Maart 1906, Dl. XIV).

C O N T E N T S.

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W. BURCK: "On plants which in the natural state have the character of ever sporting varieties in the sense of the mutation theory". (Communicated by Prof. J. W. MOLL), p. 798.

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Anatomy. — "*On the relation between the teeth-formulas of the platyrrhine and catarrhine Primates*". (Communicated by Prof. L. BOLK).

(Communicated in the meeting of March 31, 1906).

Among the anatomical characteristics by which the Primates of the New-World — the platyrrhine apes — are distinguished from those of the Old-World — the catarrhine apes and man — the composition of the set of teeth takes a first place. They are characterized because they possess in the upper and lower jaw one milk-molar with premolar, which replaces this, more than the latter.

In simplified writing the set of teeth of catarrhine Primates may be rendered by the following formula:

$$\begin{array}{r}
 2 \text{ } I. \text{ } 1 \text{ } C. \text{ } 2 \text{ } P. \\
 2 \text{ } i. \text{ } 1 \text{ } c. \text{ } 2 \text{ } m. \text{ } 3 \text{ } M. \\
 \hline
 2 \text{ } i. \text{ } 1 \text{ } c. \text{ } 2 \text{ } m. \text{ } 3 \text{ } M. \\
 2 \text{ } I. \text{ } 1 \text{ } C. \text{ } 2 \text{ } P.
 \end{array}$$

in which the teeth of the permanent set of teeth are written with a capital letter.

For the majority of the platyrrhine Primates the following formula holds true :

$$\begin{array}{r}
 2 \text{ } I. \text{ } 1 \text{ } C. \text{ } 3 \text{ } P. \\
 2 \text{ } i. \text{ } 1 \text{ } c. \text{ } 3 \text{ } m. \text{ } 3 \text{ } M. \\
 \hline
 2 \text{ } i. \text{ } 1 \text{ } c. \text{ } 3 \text{ } m. \text{ } 3 \text{ } M. \\
 2 \text{ } I. \text{ } 1 \text{ } C. \text{ } 3 \text{ } P.
 \end{array}$$

This last formula is only applicable to the family of Cebidae, whereas the Hapalidae differ from them because they have a molar less, so that the formula for their set of teeth becomes as follows :

$$\begin{array}{r}
 2 \text{ } I. \text{ } 1 \text{ } C. \text{ } 3 \text{ } P. \\
 2 \text{ } i. \text{ } 1 \text{ } c. \text{ } 3 \text{ } m. \text{ } 2 \text{ } M. \\
 \hline
 2 \text{ } i. \text{ } 1 \text{ } c. \text{ } 3 \text{ } m. \text{ } 2 \text{ } M. \\
 2 \text{ } I. \text{ } 1 \text{ } C. \text{ } 3 \text{ } P.
 \end{array}$$

The difference however in the set of teeth between Cebidae and Hapalidae is for the present of less importance, the significance of it will be shown later on. In the first place the attention should be fixed on the principal difference between all platyrrhine Primates on one side and all catarrhine ones on the other, i.e. the occurrence of only two milkmolars and premolars with these and of three milkmolars and premolars with those.

It is not doubtful that the set of teeth of catarrhine apes and of man must be deduced from one that was composed like the set of teeth of the now living Platyrrhines with three molars, so compared with the set of teeth of those, the set of teeth of the catarrhine Primates may be considered as reduced, the total number of teeth is larger with the former than with the latter. In what way has this reduction of the set of teeth come about, this is a question which has been frequently put and which has been answered in different ways. An obvious conception is certainly this, that a milkmolar with his replacing tooth, the premolar, has become lost. But which of the row has disappeared? This question has been answered in different ways. Whereas the Anthropologists in general are more of the opinion that the last milkmolar and premolar have been linked out, zoologists, palaeontologists and anatomists accept the view

that it has been the first, so that which follows immediately on the caninetooth. The two opinions have in common that they link out a milk molar and its replacing tooth from the continuity of the tooth row. On account of this the two theories may be distinguished as the excalation theories. I cannot agree with any of these opinions, it appears to me that the reduction has been brought about in another way, but this can only be explained more fully, when I shall have brought forward what pleads for and what against each of the above mentioned theories.

The Anthropologists look for their proof material, or perhaps more exactly for the arguing of their theses in the variations in the set of teeth, which occur with man. Of late DUCKWORTH among others has again drawn attention to the fact that rudiments of a tooth, more or less developed often appear between the last bicuspid tooth and the first molar tooth especially in the upper jaw and what is especially of importance, often on both sides. These rudiments are conical tooth-points, now occurring single either on the inner or the outer border of the alveolar margin, then again double on each of the two borders simultaneously. And DUCKWORTH does not hesitate to consider these rudiments as the again visible traces of the linked out third premolar: "on the whole we think that it is most reasonable to adopt the view that they are aborted third premolars, which constitute a human type of dentition similar to that of the New World Apes"¹⁾. From the investigation of DUCKWORTH the following must be mentioned. Firstly that the occurrence of these rudiments of a third premolar is exceedingly different with the different races: in 300 old Egyptian skulls he found no single case, on the other hand in some thirty skulls of Australians he found these rudiments seven times. The set of teeth of the natives of New-Britain shows this anomaly exceedingly often. With respect to the set of teeth of the Anthropoids, DUCKWORTH mentions that with seven of the thirteen skulls of gorillas, which he investigated, the rudiments in question were present whereas on the other hand he found them not a single time with *Hylobates* nor with Orang-outans or Chimpanzees.

The reasoning of those who think that the first milkmolar and premolar, following on the canine tooth have fallen out, in the passing from the platyrrhine form to the catarrhine form is of quite a different nature. It is a fact which is generally acknowledged as being true that originally the number of premolars of the primitive Primates did not amount to three but to four; so that already the

¹⁾ W. H. L. DUCKWORTH. *Studies in Anthropology*. Cambridge 1904. p. 22.

platyrrhines also, with their three premolars and milkmolars, possess a reduced set of teeth, and indeed among the group, of the primitive Primates which OSBORN puts together under the general name of + Mesodonta, forms are found with which both in upper and lower jaw still four premolars occur (+ Hyopsodus). According to the investigations of LECHE the number of four premolars has decreased to three, because the premolar which follows immediately behind the canine tooth — so the first or front of the row — has become lost. As most convincing for this opinion of LECHE the set of + Microchoerus may count, where only three premolars occur in the upper jaw, and still as many as four in the lower jaw, but of these the first of the row has been reduced to a rudiment without function. Where it is as good as proved that the reduction of four to three premolars with the primitive Primates has been brought about by the disappearance of the premolar following immediately behind the canine tooth, where moreover we know that with other animals also reduction of teeth may take place in this spot, there it is quite comprehensible that the further reduction of four to three premolars in the same place is localized. The difference between the two explained opinions is easily made recognizable by writing down the complete tooth formula of the primitive Primates and that of the now living ones.

For the primitive Primates we get the following formula in which the probably original number of *Incisivi* has not been reckoned with :

$$\begin{array}{r}
 I. \ 1. \ 2. \ C. \ 1. \ P. \ 1. \ 2. \ 3. \ 4. \\
 i. \ 1. \ 2. \ c. \ 1. \ m. \ 1. \ 2. \ 3. \ 4. \ M. \ 1. \ 2. \ 3. \\
 \hline
 i. \ 1. \ 2. \ c \ 1. \ m. \ 1. \ 2. \ 3. \ 4. \ M. \ 1. \ 2. \ 3. \\
 I. \ 1. \ 2. \ C. \ 1. \ P. \ 1. \ 2. \ 3. \ 4.
 \end{array}$$

For the Platyrrhines (Cebidae) the formula becomes :

$$\begin{array}{r}
 I. \ 1. \ 2. \ C. \ 1. \ P. \ 0. \ 2. \ 3. \ 4. \\
 i. \ 1. \ 2. \ C. \ 1. \ m. \ 0. \ 2. \ 3. \ 4. \ M. \ 1. \ 2. \ 3. \\
 \hline
 i. \ 1. \ 2. \ c. \ 1. \ m. \ 0. \ 2. \ 3. \ 4. \ M. \ 1. \ 2. \ 3. \\
 I. \ 1. \ 2. \ C. \ 1. \ P. \ 0. \ 2. \ 3. \ 4.
 \end{array}$$

According to the opinion of Anthropologists this formula becomes for the catarrhine Primates :

$$\begin{array}{r}
 I. \ 1. \ 2. \ C. \ 1. \ P. \ 0. \ 2. \ 3. \ 0. \\
 i. \ 1. \ 2. \ c. \ 1. \ m. \ 0. \ 2. \ 3. \ 0. \ M. \ 1. \ 2. \ 3. \\
 \hline
 i. \ 1. \ 2. \ c. \ 1. \ m. \ 0. \ 2. \ 3. \ 0. \ M. \ 1. \ 2. \ 3. \\
 I. \ 1. \ 2 \ C. \ 1. \ P. \ 0. \ 2. \ 3. \ 0.
 \end{array}$$

so the milkmolars and premolars of man should be the original 2nd and 3rd.

According to the theory, mentioned in the second place, the formula becomes :

<i>I.</i>	1.	2.	<i>C.</i>	1.	<i>P.</i>	0.	0.	3.	4.
<i>i.</i>	1.	2.	<i>c.</i>	1.	<i>m.</i>	0.	0.	3.	4.
<hr/>									
<i>i.</i>	1.	2.	<i>c.</i>	1.	<i>m.</i>	0.	0.	3.	4.
<i>I.</i>	1.	2.	<i>C.</i>	1.	<i>P.</i>	0.	0.	3.	4.

so that with man the original 3rd and 4th milkmolar and premolar would still exist.

The last mentioned opinion seemed to me also to be the most acceptable. It pleads for it, that in a phylogenetically older stadium the first milkmolar and its premolar had already become lost, and if then one lets the second follow, the reduction-process is localized and more continuity brought into it. The following can moreover be said against the opinion of the Anthropologists, that the fourth milkmolar and premolar with man should have been lost. It may be justly supposed that only those teeth can reduce, which fulfill the smallest function. And this now does not apply to the last milkmolar and premolar. On the contrary. With the *Platyrrhines* we see, that just that last molar does not only not stay behind by the others, but is even the strongest developed of the three. So with those forms, where we might with some right suppose at least some indication to a reduction of this tooth, we on the contrary find a progressive development. No single reason can be given why in the middle of this toothrow a tooth should suddenly have disappeared, and why a discontinuity of the set of teeth should have come about by which the function would have suffered considerably, no single indication can be found, neither in the ontogenetic nor in the full-grown set of teeth, in the form of a diastem, that a tooth has really become lost here, and so the first mode of explanation : that the last milkmolar and its replacing tooth would have become lost, does not seem probable to me.

But neither can the theory that at the passing from the *platyrrhine* to the *catarrhine* type, the first milkmolar with the premolar belonging to it, should have been linked out, satisfy me. The above mentioned argument about it, is always only an argument per analogiam without its being possible that a morphological proof for such a reduction can be given. If the sets of teeth of *Platyrrhines* are compared in particular with relation to the degree of development of the first premolar nothing is found that points to a reduction of this

tooth, at least with the now living forms; on the contrary, the first premolar is often stronger than the second (*Cebus*, *Chrysothrix*, *Mycetes*, *Hapale*). Then not a single indication can be observed in the Ontogenese of the set of teeth of man, which indicates that a tooth should have become lost behind the canine tooth, the papillae succeed each other very regularly in their origin and place. Moreover if it were right that a molar and a premolar became lost behind the canine tooth the remarkable fact remains still unexplained, that a rudimentary tooth appears so often between the first molar and the last premolar.

So I cannot agree with either of the two opinions which prevail now about the differentiation of the set of teeth of the Primates, but I am of the opinion that it came about in quite another way. To be short, my opinion about it is as follows: the set of teeth of the catarrhine Primates has originated from that of the platyrrhines by the disappearance of the last or third molar and of the last or third premolar while the third milkmolar has lost its character of temporary tooth and has become a permanent tooth.

This opinion is explained by the two following formulas. If we overlook the original number of four milkmolars and premolars, and number the elements of the platyrrhine set of teeth according to their now present amount this set of teeth may be written according to the following formula:

$$\begin{array}{ccccccc} I_1. & I_2. & C. & P_1. & P_2. & P_3. & \\ i_1. & i_2. & c. & m_1. & m_2. & m_3. & M_1. & M_2. & M_3. \\ \hline i_1. & i_2. & c. & m_1. & m_2. & m_3. & M_1. & M_2. & M_3. \\ I_1. & I_2. & C. & P_1. & P_2. & P_3. & \end{array}$$

The catarrhine set of teeth has originated from this, as P_3 and M_3 have fallen away in the upper and lower jaw, whereas m_3 becomes M_1 in both jaws, by which as a matter of course M_1 of the platyrrhines becomes M_2 of the catarrhines, the M_2 of the former becomes M_3 of the latter. If it had remained the M_2 of the platyrrhines would have become M_4 of the catarrhines. Those things are stated in the following formula in which the reduced teeth are put between parenthesis.

$$\begin{array}{ccccccc} I_1. & I_2. & C. & P_1. & P_2. & [P_3]. & \\ i_1. & i_2. & c. & m_1. & m_2. & M_1. & M_2. & M_3. & [M_4]. \\ \hline i_1. & i_2. & c. & m_1. & m_2. & M_1. & M_2. & M_3. & [M_4]. \\ I_1. & I_2. & C. & P_1. & P_2. & [P_3]. & \end{array}$$

So the differentiation of the set of teeth of the Primates is accord-

ing to my view more complicated than would have been the case according to the two above mentioned exclamation theories. Two phenomena may be distinguished in this process of development, namely progressive development of one of the elements: m_2 loses its character of temporary element and becomes persistent, and the second phenomenon is the reduction of two other elements. These two elements are at the extremity of each of the two tooth series, P_2 at the end of the series of replacing teeth, M_2 of the end of the series of the teeth of the first generation. Contrary to the two above mentioned exclamation hypotheses I might distinguish the one defended by me as the hypothesis of the terminal reduction. I shall try to show the correctness of my opinion.

If I let m_2 of the Platyrrhines become a persistent tooth, no new principle is introduced into odontologie. For it is known to us from other groups of animals that milk teeth may become persistent teeth; I remind the reader of the Marsupialia, where but for some exceptions the whole set of milk teeth has become a set of persistent teeth except a single tooth. Furthermore to Erinaceus, where according to the investigations of LECHER the so called persistent set of teeth consists partly of milk teeth partly of permanent teeth. So my opinion is nothing more than a new example of the tendency also observed elsewhere of a diphyodont set of teeth to pass into a monophyodont. So against the principle as such there can be no objection.

As a first argument for the correctness of my opinion I state the morphology of the milk molars in platyrrhines, I had the opportunity of studying them from Hapale, Chrysothrix, Cebus, Mycetes, Pithecia and Ateles. Without going into details it must only be mentioned here that m_2 of the platyrrhines differs a great deal both in the composition of its crown and in the number of its fangs from m_1 or m_3 , and shows much resemblance to M_1 of these apes.

It is of much importance with this that m_2 is functionally a higher developed tooth than its deciduous tooth P_2 , so that means that at the moment that m_2 is replaced by P_2 , the set of teeth becomes to a certain degree functionally inferior. So if m_2 becomes persistent, this means a gain for the mechanism of the set of teeth. This does not hold true for m_1 and m_3 , the replacing P_1 and P_3 are functionally higher developed.

A second motive is derived from the development of the set of teeth of the catarrhine Primates, in particular that of man. So according to my opinion our first molar has passed from a milk tooth into a persistent tooth in a relatively recent stadium, with the Platyrr-

rhines it still belongs to the milk teeth. May this not be the explanation of the fact that our first molar still breaks through in connection with the teeth of the set of milk teeth, and still before the appearance of the first replacing tooth, while the second tooth appears only after a period of some years? By this early appearance of our first molar it functionates indeed for some time together with the complete set of milk teeth and so according to my opinion the set of teeth of man still possesses in this period a composition as in the first lifetime of the Platyrrhines. Still more distinctly than from the time of the eruption this relation appears when the first forming during the ontogenese is more closely investigated. I derive the following about this from the wellknown investigation of Rösse ¹⁾. Between the 9th and 12th week of the faetal development the papillae of the milk teeth are invaginated in the dental band (Zahnleiste) which grows on uninterruptedly towards the back, and already in the 17th week of the development the papilla of the first molar is invaginated. So with man there is not the least histogenetical discontinuity between the forming of the milk teeth and of the first molar. Only after the course of a year, so four months after the birth the dental band begins to grow on towards the back and not before the 6th month after birth the papilla of the second tooth is invaginated. So while M_1 is formed immediately after m_1 with man, a pause of about a year begins after this first development. So both from morphology and ontogeny arguments may be derived for the hypothesis that m_1 of the Platyrrhines is homological to M_1 of the Catarrhines.

My hypothesis however still contains another element viz. the reduction of P_3 and M_3 of the Platyrrhines.

Let us first consider the reduction of M_3 . From my above mentioned deduction of the catarrhine set of teeth given in a formula, follows that I come in conflict with a rather generally accepted opinion that the three molars of the Catarrhines should be homologue to the three molars of the Platyrrhines. According to my opinion M_1 of the Platyrrhines is homologue to M_3 of the Catarrhines, M_2 of those homologue to M_2 of these, and in the set of teeth of the Catarrhines the homologon of M_3 of the Platyrrhines is wanting. If this tooth should also appear by the last mentioned group of Primates it would become a M_4 . Now it is a fact that is universally known that a more or less developed fourth molar is not seldom with man and among the Anthropoids, especially

¹⁾ G. Rösse, Ueber die Entwicklung der Zähne des Menschen. Arch. f. mikrosk. Anat. Bnd. XXXVIII.

with the Orang and Gorilla. Moreover ZUCKERKANDL¹⁾ has shown that the epithelial rudiment of a fourth molar of man is formed with the majority of the individuals. This rudiment of a tooth and the eventual eruption of the fourth molar were till now phenomena which were somewhat difficult to interpret. There was an inclination to keep this fourth molar with man for an atavism and the set of teeth of man was deduced from a hypothetical primitive form when the set of teeth contained four molars. Here however the difficulty offers itself that among the already numerous well known primitive Primates there has never been found a form with four molars. ZUCKERKANDL also reveals this difficulty where he points to it that four molars should only appear with the primitive forms of the carnivores. SELENKA²⁾ also, who found from his rich material that with Orang in 20% of the cases appears a fourth molar feels the mentioned difficulty and interprets the variation in another way. It should not be atavism but a progressive phenomenon in that sense, that the set of teeth of Orang is on the way of bringing into development a fourth molar. It appears to me that this explanation of SELENKA is not correct. If this variation were only known to us from Orang, no direct difficulties could be stated against this hypothesis. But such a fourth molar also occurs as I said before very often with man. And now it is not doubtful that the extremity of the human set of teeth is in a state of regression, the third molar is always more or less reduced and even according to the investigations of DE TERRA³⁾ and others issues no more with at least 12 % of the recent Europeans. Where it is now fixed that our set of teeth reduces at its extremity, the formation and issue of a fourth molar can hardly be interpreted as a progressive phenomenon.

The hypothesis brought forward by me gives a simple solution of the difficulty. The fourth molar of man and of the Anthropoids is indeed an atavism but does not refer back to a removed primitive form unknown to us, but does not go any farther than to the nearest past of the history of development of our set of teeth, it is the homologon of M_4 of the Platyrrhines. And contemplated in such a way the relatively frequent occurrence of it can no longer surprise us.

¹⁾ E. ZUCKERKANDL, Vierter Mahlzahn beim Menschen. Sitzungsber. der k. Akad. d. Wiss. Wien Bnd. C.

²⁾ E. SELENKA. Menschenaffen. Rassen, Schädel und Bezeichnung des Orang Utan. Wiesbaden 1898.

³⁾ M. DE TERRA. Beiträge zu einer Odontographie der Menschenrassen. Zürich 1905.

More direct proofs may however be cited for the conclusion that M_2 of the Platyrrhines should be reduced. For if the sets of teeth of different representatives of this group are investigated, it is undeniable that M_2 is behind in development to M_2 and M_1 .

Not all Platyrrhines are alike in this regard, with some species the set of teeth is apparently very constant with other it is more variable. A particularly fixed set of teeth *Chrysothrix* seems to possess. I could at least find not a single deviation in the 130 skulls of *Chrysothrix sciurea* which I possess, no more in 60 skulls of *Cebus fatuellus*, although the M_2 is already very much reduced with this species. *Ateles* on the contrary seems to possess a set of teeth which is richer in variations and BATESON¹⁾ mentions three cases in which the M_2 which is already reduced in this genus quite fails. The mentioned author points to it that in these cases *Ateles* possessed a formula for its set of teeth which is typical for the second family of the Platyrrhines — the Hapalidae. And in connection with this I may now examine the set of teeth of the Hapalidae in the light of my hypothesis. This hypothesis puts that M_2 of the Platyrrhines became lost in passing to the catarrhine type, that m_2 becomes M_1 and that P_2 no longer issues. Where a reduction of M_2 is not seldom found with the Cebidae, and now and then even it is quite wanting as an individual variation, there M^2 is already constantly absent with the Hapalidae. So with these Platyrrhines one phase of the process has already been run through, but not yet the second phase, the progression from m_2 to M_1 . So according to my opinion the set of the Hapalidae does not stand as a deviating form at the side of that of the other Platyrrhines, but must be considered as an intermediate form, between the original platyrrhine and the definite catarrhine set of teeth.

So we see that several phenomena plead for my opinion, that the catarrhine set of teeth has not originated by an exclamation but by a terminal reduction, and I must stop at my assertion that, because m_2 has become M_1 the replacing tooth, which originally belonged to it, i.e. P_2 no longer appears.

By this supposition, the observation of the anthropologists is done justice to, that a rudimentary tooth does relatively often appear with man and Gorilla between P_2 and M_1 . When P_2 has only been suppressed as a normal element of the set of teeth, in a relatively recent period of the development, than the supposition lies at hand, that this tooth also like M_2 of the Platyrrhines ontogenetically will be formed

¹⁾ W. BATESON. Materials for the Study of Variation. London, 1894.

still. And it is my opinion that the rudiments of a tooth which so often occur in the indicated place are indeed traces of the P_1 which has got lost.

There could still be mentioned some more anomalies in the set of teeth of man (the growing together of M_1 with a superfluous tooth, the pushing out of M_1 and replacing by a new tooth (so called third dentition) which would be explained by my hypothesis, but I will not look more closely into this matter in this place.

By my opinion about the differentiation of the set of teeth of the Primates I come into conflict with a rather universally prevailing opinion about the morphological significance of the first molar of the Placentalia. This molar is universally considered with all Placentalia as a perfectly homological element of the set of teeth. Thus says SCHLOSSER¹⁾ e. g. speaking of the first molar of man: "Niemand wird sicher die Homologie dieses Zahnes mit dem ersten Molaren der übrigen Placentaler bestreiten dürfen". Where I now homologise M_1 of man with m_1 of the Platyrrhines I come into conflict with this opinion. If we however try to find motives for the above mentioned opinion in literature, we seek in vain. And so it seems to me, that here we have to do with a dogma, which is not without danger for the comparative anatomy of the set of teeth. For it lies at hand that as soon as in the whole row of the Placentalia one element of the set of teeth is fixed in its morphological significance, that then the homologating of the other elements must join itself to this aprioristical principle. And where such a thing is possible to a certain degree with a canine tooth, which is sharply distinguished from the other teeth by its peculiar form, it is absolutely impossible with a definite molar which possesses no specific morphological qualities.

I cannot finish this communication before having pointed to a phenomenon, which is immediately related to the here communicated point of view. If we compare the set of teeth of man with that of the other catarrhine Primates, it appears that the process, by which the catarrhine set of the teeth originated from the platyrrhine type, is still progressive with man, and that the human set of teeth is on its way to differentiate from that of the other Catarrhines in the same way, as these differentiated from the Platyrrhines one time. I shall try to show this in short. The still active differentiation of the human set of teeth appears from different facts. First as to the premolars. In comparison to all other Primates the premolars of men

¹⁾ M. SCHLOSSER. Das Milchgebiss der Säugetiere. Biol. Centralblatt, Bnd. 10, blz. 89.

have been reduced considerably, and the 2nd premolar more than the first. Where as the premolars in the upper jaw of all other Catarrhines possess three and in the lower jaw two fangs, the premolars of man have normaliter one single fang. That this has originated from several, appears from the grooves on the surface. Now it is not without significance that the first premolar shows its origine of a form with several fangs, by a dividing of the point of the fang. So P_2 is more reduced than P_1 with man. If further the milkmolars, which temporarily precede the premolars are compared, we state that the milkmolars differentiate progressively in the group of the catarrhines, and this is especially the case with the second milkmolar. The progression concerns especially the crown of the teeth, the number of roots is two in the lower jaw, three in the upper jaw.

So if we for a moment fix our attention exclusively on m_2 and its replacing tooth P_2 with man, it appears that the first is in progression, the second in regression, and that with man, the same relation exists in regard to these two teeth as with m_2 and P_2 of the Platyrrhines. When man namely pushes out his m_2 and replaces it by P_2 , his set of teeth becomes functionally inferior, for instead of a tooth with five or four knobs on the crown and two or three fangs there comes in its place a tooth with two cusps on the smaller crown and only one root.

So we see, that the terminal element of the dental band of the second generation (P_2) reduces with man. Still distinctly may be seen the terminal reduction of the tooth band, of the first generation, closing with M_2 , for as is already mentioned our M_2 no longer even issues in $\pm 12\%$ of all cases, and is always behind in development, at least with more highly developed human races. So the human set of teeth is characterized from the catarrhine Primates by the following peculiarities; the last molar is on its way of reduction, the last premolar is on its way of reduction, the last milkmolar has developed very progressively. So a trio of phenomena which are entirely homological to those, by which the catarrhine set of teeth has originated from the platyrrhine. Only one phase is still wanting to the process, namely the remaining persistent of the last milkmolar and the suppression of the last premolar. And this phase also is reached now and then individually. This among others appears from what MAGITOT says: La persistance des grosses molaires temporaires (m_2) s'observe très-souvent, concurremment avec l'absence congénitale ou l'atrophie des secondes prémolaires (P_2)

Nous en connaissons de nombreux exemples¹⁾. If the stated phenomena are connected with each other the conformity to the earlier process of development of the set of teeth of the Primates as I take it, immediately strikes the eye; and one would be inclined to this thesis; In the future set of teeth of man P , will no longer erupt, m , will have become persistent and functionate as M_1 , but by the simultaneous reduction of M , the number of molars will not have become larger than three.

So from this communication appears that the differentiation of the entire set of teeth of the Primates is from my standpoint more intricate than was supposed till now, but it seems to me that my principle of the terminal reduction can better be brought into accordance with the function of the set of teeth, and is based on a larger number of facts than the hypothesis of the exclamation. What from a general point of view, also seems to me to plead for my opinion is the fact, that in the exposition given by me the development of the set of teeth has taken place without a discontinuity in the toothrows at any time.

Physics. — *“A simple geometrical deduction of the relations existing between known and unknown quantities, mentioned in the method of VOIGT for determining the conductivity of heat in crystals. By Dr. F. M. JAEGER. (Communicated by Prof. P. ZEEMAN.)”*

(Communicated in the meeting of March 31, 1906).

It is commonly known that about ten years ago W. VOIGT²⁾ indicated a method, based on a recognized principle of KIRCHHOFF, by which to determine the relative conductivity of heat in crystals in the different directions. His mode of experimental examination consists in the determination of the break which two isothermal lines present at the boundary line of an artificial twin, the principal directions of which form a given angle φ with that line, whilst the conduction of heat takes place along the line of limit. The isothermal lines are rendered visible to the eye by the tracings formed by the fusion of a mixture of elaidic acid and wax with which the plane of the crystal has previously been covered.

¹⁾ E. MAGIROT. *Traité des Anomalies du Système dentaire*. Paris 1877. p. 221.

²⁾ VOIGT, *Göttinger Nachrichten*, 1896, Heft 3.

The method of VOIGT is far more accurate than that of DE SÉNARMONT¹⁾ or even of RÖNTGEN²⁾, and, requiring for other purposes to investigate the relative conductivity of heat in crystals, it was obvious that I should make use of the method indicated by VOIGT.

For a crystal, for which the rotatory coefficients, found in accordance with the theory of G. C. STOKES³⁾, are = 0, VOIGT deduces the relations required here by constructing the equations of the flow of heat, conformable to the conditions of limit which are common to the lateral boundaries of both plates; i.e. that *along* that line the loss of temperature must be the same, and moreover that in a direction normal to that boundary-line the entire flow of heat must be the same in the two contiguous plates.

Prof. LORENTZ had the kindness to derive the above mentioned relations in an analogous manner and to note down the conditions under which the break in the isothermal lines will reach its maximum.

If ϵ be the break, and ϕ the angle, formed in the plates by the two principal directions, is 45° , the proportion of the two coefficients of the conduction of heat in those directions, consequently $\frac{\lambda_1}{\lambda_2}$ is found as follows:

$$tg\epsilon = (\lambda_1 - \lambda_2) \frac{(\lambda_1 + \lambda_2)}{2\lambda_1\lambda_2}.$$

If ϕ differs from 45° , VOIGT finds in that case:

$$tg\beta = \frac{(\lambda_1 - \lambda_2) \sin 2\phi}{(\lambda_1 + \lambda_2) - (\lambda_1 - \lambda_2) \cos 2\phi},$$

which for ϕ equal to 45° passes into the formula of Prof. LORENTZ by introducing $tg \frac{\epsilon}{2}$ ($= tg\beta$ according to VOIGT's deduction) instead of $tg\epsilon$.

Instead of the complicated formulæ which are required for the determination of these relations, we here give a simple geometrical demonstration, which, besides presenting $\frac{\lambda_1}{\lambda_2}$ in a form which is immediately available for logarithmic calculations, possesses at the same time the advantage of being easily discernible.

If, from a given point O in the centrum of a crystal, a flow of heat can take place without interruption in all directions, the isothermal

¹⁾ DE SÉNARMONT, Compt. rend. **25**, 459, 707. (1847).

²⁾ RÖNTGEN, Pogg. Ann. **151**, 603, (1874).

³⁾ STOKES, Cambr. and Dublin Math. Journal. **6** 215, (1851).

surfaces in a similar plane of a crystal are, in most cases, concentric and equiform three-axial ellipsoids whose half axes stand in the relation of $\sqrt{\lambda_1}$, $\sqrt{\lambda_2}$ and $\sqrt{\lambda_3}$; among these the so-called principal ellipsoid h , whose axes are $\sqrt{\lambda_1}$, $\sqrt{\lambda_2}$ and $\sqrt{\lambda_3}$ must here be kept more especially in view.

In the present case we leave unnoticed the rotatory qualities of the crystal, and suppose an infinitely thin plate, cut parallel to a plane of thermic symmetry, whose principal directions correspond to the coordinate axes. Let fig. 1 represent the elliptic intersection of the plate with the ellipsoid h ; the line traced by the melted wax then has the direction of the tangent of the ellipse in the point $P(x'y')$, given by the radius vector ρ , which may enclose the angle φ with the axis X . The flow of heat may thus proceed along ρ , being the boundary line. In this case the equation for the isothermal line pq is:

$$\frac{xx'}{\lambda_1} + \frac{yy'}{\lambda_2} = 1.$$

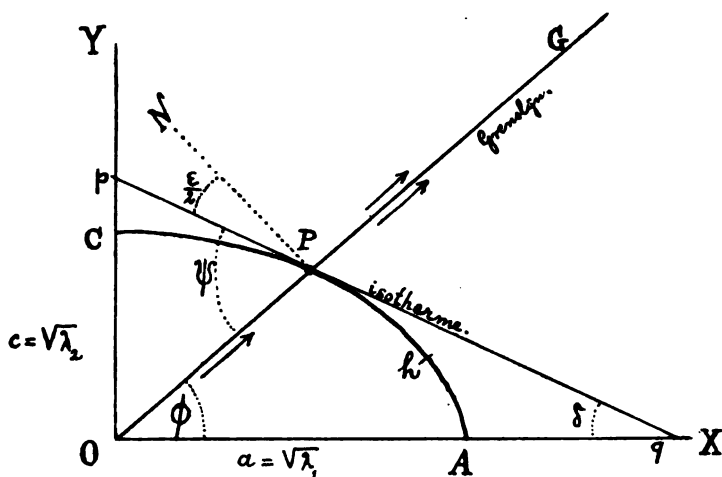


Fig. 1.

Thus for the two sections Op and Oq cut off on the two axes the result is:

$$Op = \frac{\lambda_2}{y'} = \frac{\lambda_2}{\rho \sin \varphi}$$

$$Oq = \frac{\lambda_2}{x'} = \frac{\lambda_1}{\rho \cos \varphi}$$

therefore :

$$\frac{Op}{Oq} = \frac{\lambda_2}{\lambda_1} \cot \varphi.$$

On the other hand however :

$$\frac{O_p}{O_q} = \operatorname{tg} \delta = \operatorname{tg} \left\{ 90^\circ - \left(\varphi + \frac{\varepsilon}{2} \right) \right\} = \cot \left(\varphi + \frac{\varepsilon}{2} \right),$$

where $\frac{\varepsilon}{2}$ is half of the break of the isothermal lines at the boundary line OG .

The immediate conclusion is therefore :

$$\frac{\lambda_1}{\lambda_2} = \operatorname{tg} \left(\varphi + \frac{\varepsilon}{2} \right) \cot \varphi \dots \dots \dots (A)$$

From this equation the required proportion may be at once deduced when φ represents the direction of the plate and the value of ε has been ascertained.

Moreover it will be easy to find the maximum of ε — and thus reduce the errors of investigation to the lowest figures. Suppose $A = \frac{\lambda_1}{\lambda_2}$, the above stated formula, after a few goniometrical transformations becomes :

$$\operatorname{tg} \frac{\varepsilon}{2} = \frac{(A-1) \sin 2\varphi}{(A+1) - (A-1) \cos 2\varphi}.$$

This function will be a maximum for $\frac{d\varepsilon}{d\varphi} = 0$, i. e.

$$\frac{d\varepsilon}{d\varphi} = \frac{2 \{ (A^2 - 1) \cos 2\varphi - (A-1)^2 \}}{(A^2 + 1) - (A^2 - 1) \cos 2\varphi} = 0.$$

The maximum condition then becomes :

$$\cos 2\varphi = \frac{A-1}{A+1} = \frac{\lambda_1 - \lambda_2}{\lambda_1 + \lambda_2},$$

and the appertaining maximum break ε in the isothermal lines is then expressed by :

$$\operatorname{tg} \frac{\varepsilon}{2} = \frac{(\lambda_1 - \lambda_2)}{2 \sqrt{\lambda_1 \lambda_2}} \dots \dots \dots (B)$$

In cases where the difference between $\sqrt{\lambda_1}$ and $\sqrt{\lambda_2}$ is very small — and observation teaches that this is usually the case — the notation may be :

$$\operatorname{tg} \frac{\varepsilon}{2} = \frac{\lambda_1 - \lambda_2}{\lambda_1 + \lambda_2} \dots \dots \dots (C)$$

For practical purposes therefore, the theoretical maximum $\varphi = 45^\circ$ may be taken as fairly accurate, so that then the twin plate with

the isothermal lines etc., takes the form of fig. 2. In that case it follows from A :

$$\frac{\lambda_1}{\lambda_2} = \operatorname{tg} \left(45^\circ + \frac{\varepsilon}{2} \right) (D)$$

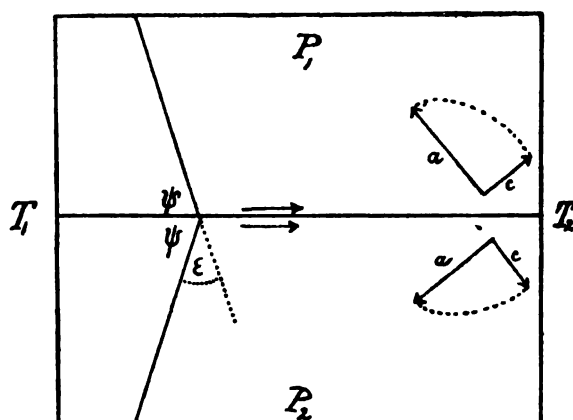


Fig. 2.

By expressing $\operatorname{tg} \varepsilon$ as a function of $\operatorname{tg} \frac{\varepsilon}{2}$ from (C) one obtains the relation deduced by Prof. LORENTZ;

$$\operatorname{tg} \varepsilon = (\lambda_1 - \lambda_2) \frac{(\lambda_1 + \lambda_2)}{2 \lambda_1 \lambda_2}.$$

Moreover from the geometrical solution here given the fact is again brought to light that in general the angle ψ is not equal to 90° ; in other words in this simple but experimental way is proved by ocular demonstration the truth of the statement already made by VOIGT, that the isothermal lines in crystals do not generally stand perpendicular to the direction of the flow of heat.

Along the thermic axes however this is the case, because the tangent lines at the ellipses are there directed perpendicularly to these axes.

From fig. 1 also follows the form of the break as a result of $\lambda_1 > \lambda_2$.

I hope soon to communicate the results obtained in the measurement of crystals by means of this method, together with a few observations on the differences of these results with those, derived in the same minerals by the usual methods of DE SÉNARMONT and RÖNTGEN.

Botany. — “*On plants which in the natural state have the character of ever-sporting varieties in the sense of the mutation theory.*”

By Dr. W. BURCK. (Communicated by Prof. J. W. MOLL).

(Communicated in the meeting of March 31, 1906).

An investigation of the causes of Cleistogamy ¹⁾ showed that: 1 plants with closed flowers originated by mutation from plants with chasmogamic flowers and 2 that they occur in the natural state, partly as constant, partly as ever-sporting varieties.

In the course of this investigation the question arose whether other wild-growing plants do not also have the character of ever-sporting varieties.

Especially those plants were thought of that have bisexual and unisexual flowers in one and the same individual or in which by the side of bisexual, unisexual individuals are found and also those plants among the dioecious ones that possess rudimentary stamens or ovaries, from which may be inferred that they originated from plants with bisexual flowers.

The agreement between unisexual, cleistogamic and filled flowers pointed to the same origin, while the resemblance in the manner in which unisexual flowers occur among the hermaphrodite ones and closed flowers among the chasmogamic ones, justified the assumption that in the monoecious and dioecious as well as in the cleistogamic we have ever-sporting and constant varieties.

This summer I tried to confirm this conception in a twofold manner, firstly by cultivating the gyno-monoecious *Satureja hortensis* and secondly by studying the different forms in which one and the same andro-monoecious Umbellifer can occur in nature with regard to the number of male flowers in proportion to that of the bisexual ones and to the place which the male flowers occupy on the principal and secondary axes.

To the results of the culture experiments I shall return afterwards when I shall have had an occasion to repeat these experiments on a larger scale and with more species. I will here only mention that they showed that a gyno-monoecious *Satureja hortensis* begins its period of flowering with producing bisexual flowers only, that not until later, when the plant has grown stronger, a few female flowers appear among the bisexual ones, that their number gradually increases

¹⁾ Die Mutation als Ursache der Kleistogamie. Recueil des Travaux Botaniques Néerlandais Vol. II. 1905.

in the following days until a definite maximum is reached, after which it gradually decreases again until at the end of its flowering-period the plant again produces bisexual flowers only.

Hence the female flower follows the law of periodicity established by DE VRIES for the occurrence of anomalies of various nature with other plants and it may in this respect be put on a line with such anomalies. It may be compared with the increased number of leaflets of *Trifolium pratense quinquefolium*, with the filled flowers of *Ranunculus bulbosus semiplenus*, with the ramified spikes of *Plantago lanceolata ramosa*, etc.

In what follows I shall give the results obtained with the andro-monoecious Umbelliferae.

The investigations of BEIJERINCK ¹⁾, SCHULZ ²⁾, KIRCHNER ³⁾, MAC LEOD ⁴⁾, LOEW ⁵⁾, WARNSTORF ⁶⁾, and others on the sexual relations of the Umbelliferae have shown that by far the most species are andro-monoecious and that besides in some of them forms occur with female or with female and asexual flowers. Male flowers appeared in this family to be as common as bisexual ones. Male individuals are rare, however. Until now *Trinia glauca* was considered the only Umbellifer in Europe, known in the male form. From SCHULZ's notes it appears, however, that in the environs of Halle a. S. also male plants of *Oenanthe fistulosa* ⁷⁾ and *Sium latifolium* ⁸⁾ occur, while in this country also *Heracleum Sphondylium* can occur in the male form.

Far less general are female flowers. SCHULZ only mentions them for (*Eryngium campestre*)? ⁹⁾, *Trinia glauca*, *Pimpinella magna*,

¹⁾ BEIJERINCK, Gynodioecie bei *Daucus Carota* L. Nederlandsch Kruidkundig Arch. Tweede serie 4e Deel 1885, p. 345.

²⁾ AUGUST SCHULZ, Beiträge zur Kenntniss der Bestäubungseinrichtungen und Geschlechtsvertheilung bei den Pflanzen. Bibliotheca botanica. Bd. II 1888, Heft 10 und Bd. III 1890, Heft 17.

³⁾ O. KIRCHNER, Flora von Stuttgart und Umgebung 1888.

⁴⁾ J. MAC LEOD, Over de bevruchting der bloemen in het Kempisch gedeelte van Vlaanderen. Botanisch Jaarboek Dodonaea 1893 en 1894.

⁵⁾ E. LOEW, Blütenbiologische Floristik des mittleren und nördlichen Europa sowie Grönlands. 1894.

⁶⁾ C. WARNSTORF Blütenbiologische Beobachtungen aus der Ruppiner Flora im Jahre 1895. Verhandlungen des botanischen Vereins der Provinz Brandenburg Bd. XXXVIII. Berlin 1896.

⁷⁾ SCHULZ, Beitr. I p. 47.

⁸⁾ SCHULZ, Beitr. I p. 48.

⁹⁾ In his note concerning this plant on page 42 of his first paper, female flowers are not mentioned. So this is perhaps an error in the general summary at the end of the second paper.

P. saxifraga and *Daucus Carota*, for which latter plant BEJERINCK had already found them before.

In the long list of 66 European Umbelliferae in the Blütenbiologische Floristik of LOEW no more than 16 species occur that are only known as bisexual plants whereas 40 are andromonoecious. It has appeared since that with three of the plants mentioned as bisexual also male flowers are found. Of *Anethum graveolens*, *Aethusa Cynapium* and *Heracleum Sphondylium* namely, WARNSTORF found andromonoecious forms in the environs of Neu-Ruppin; also in this country they occur in this form. Of the 66 Umbelliferae that were studied, the following remain of which until now no other than bisexual plants are known:

Laserpitium pruthenicum, *Peucedanum venetum*, *Crithmum maritimum*, *Silaus pratensis*, *Seseli Hippomarathrum*, *S. annuum*, *Anthriscus vulgaris*, *Bupleurum longifolium*, *falcatum*, *tenuissimum* and *Pleurospermum austriacum*, to which list I think must be added: *Eryngium maritimum*, *Berula angustifolia*, *Conium maculatum* and *Helosciadium nodiflorum*.

It is probable that of some of these plants andro-monoecious forms will be found when they are examined over a larger part of their region of occurrence, especially since it has appeared that the different forms in which Umbelliferae can occur, are often spread over very different and widely distant parts, so that, even though the species mentioned be only known as hermaphrodite plants in a part of Europe, the possibility must be granted that they occur in other forms elsewhere.

Of *Sium latifolium* e. g., no other but the andro-monoecious form is found in a great part of Middle Europe and until now only in the environs of Halle a/S accompanied by the male form, evidently only in a few specimens. Only in our country the bisexual form is known.

Of *Pimpinella magna* the bisexual plant is only found in southern Tyrol and Italy; the andro-monoecious on the other hand in the whole of Middle Europe, while in southern Tyrol and Italy the same plant also occurs with female and with female and asexual flowers.

Of *Oenanthe fistulosa* the andro-monoecious plant is found everywhere, the male one until now only in the environs of Halle.

Of *Aethusa Cynapium* the hermaphrodite plant is known in the whole of Middle Europe, the andro-monoecious one only in the neighbourhood of Neu-Ruppin and of my residence.

Of *Daucus Carota* the andro-monoecious form is generally found,

the bisexual one until now only in Flanders¹⁾ and in this country²⁾).

So it is not at all unlikely that of those species which until now are known as bisexual only, later other forms will also be found, and similarly it may be assumed that of the large number of Umbelliferae of which now only the monoecious form is known, on closer examination also the hermaphrodite or unisexual forms will be found.

Meanwhile it is a very remarkable fact that by far the most Umbelliferae are andro-monoecious and that exactly these forms are most generally spread.

Where male individuals are found they only occur in very limited numbers as rare occurrences among the great majority of andro-monoecious individuals.

This also holds for the hermaphrodite plants, at any rate for *Daucus Carota*, *Sium latifolium* and *Heracleum Sphondylium*. Where these and andro-monoecious plants occur together the number of bisexuals is far less than that of the andro-monoecious ones.³⁾

This general occurrence of andro-monoecious forms gives a very peculiar character to the family of the Umbelliferae. Nowhere in the vegetable kingdom these forms are so prominent as here.

In other families with species that are rich in forms, as the *Labiatae*, *Alsineae*, *Sileneae* and others, where gyno- and andro-monoecious and female and male forms occur together with bisexual ones, a similar preponderance of monoecious plants is not found with a single species.

The rule is there that where the three forms occur together the monoecious flowers are a minority with respect to the bisexual and unisexual ones.

Next is conspicuous with the monoecious Umbelliferae the great variety that may be observed in the occurrence of the male flowers in the umbels of different order and the many mutually different forms in which consequently one and the same andro-monoecious plant may occur.

Sometimes an individual is found which among the large number of bisexual flowers has a relatively small number of male ones, another time one in which the number of male flowers is not much

¹⁾ J. STAES. De bloemen van *Daucus Carota* L. Botanisch Jaarboek, Dodonaea Jaargang I. 1889. p. 132.

²⁾ I shall soon treat elsewhere the different forms in which the Umbelliferae, occurring in this country, are met.

³⁾ Male Umbelliferae and exclusively bisexual species are very rare also outside Europe. (See DRUDE Umbelliferae. ENGLER und PRANTL. Die natürl. Pflanzenfamilien III. Teil. Abt. 8. p. 91).

less than that of the bisexual ones, and then again an individual in which the male flowers are more numerous than the others, and between these a long series of gradual transitions and intermediate forms is found.

Not unfrequently the number of male flowers is greatly in excess of the bisexuals. I met in this country plants of *Heracleum Sphondylium* in which the inner umbellules of the umbel of the first order and all other umbels of higher order were exclusively male and similar plants are also found of *Pastinaca sativa* and *Daucus Carota*. They are found spread among other individuals in which the proportion of male to bisexual flowers is more favourable to the bisexuals or where the number of males is even very small.

Some Umbelliferae are only known in an almost male form. *Echinophora spinosa* e. g. has one bisexual flower in the middle of the umbel; all other flowers are male. Also with *Meum athamanticum* and *Myrrhis odorata* we may observe in the specimens cultivated in this country in botanical gardens, how also there the bisexual flower is superseded, so that the umbellules often do not contain more than one such flower.

An investigation of the andro-monoecious Umbelliferae shows us at once that there is a certain regularity in the way in which the male flowers occur. In the first place, when they appear for the first time in an umbel of a certain order, their number as compared with that of the bisexual flowers increases as we come to umbels of higher order; and secondly, if in the peripheral umbellules some male flowers occur among the bisexual ones, their part in the constitution of the umbellules becomes greater as the umbellules are more distant from the periphery.

Of *Daucus Carota*, *Pastinaca sativa* and *Heracleum Sphondylium* whole series of specimens may be collected in the neighbourhood of my residence, beginning with such which in all the umbels contain only bisexual flowers up to forms which are almost or entirely (*H. Sphondylium*) male. Among these specimens are found in which the male flowers already appear in the very first umbel of the plant by the side of other specimens in which the andro-monoecious character only appears in the umbels of the second order or later still in those of the third or fourth order. Now it is a constant rule that if they appear for the first time in an umbel of a certain order they will also appear in the umbels that develop later and that their number in proportion to that of the bisexual flowers in the successive umbels goes on increasing.

Specimens which in no respect revealed their andro-monoecious character during the whole summer, which only late in summer produced male flowers in the umbels of the third or fourth order or sometimes entire male umbels, are found connected by intermediate forms with specimens which already in the very first umbels contain male flowers.

Concerning the part occupied by male flowers in the constitution of the peripheral and central umbellules, it must be remarked in the first place that with all Umbelliferae whose umbels reach a certain size, the peripheral umbellules consist of a larger number of flowers than those that occupy the middle part of the umbel. In some species those central umbellules may be very poor in flowers; with *Daucus Carota* the central umbellules often even consist of only one flower.

When it was stated that the part occupied in the umbellules by the male flowers becomes greater the more they are placed near the centre of the umbel, this must be so understood that as the umbellules become more distant from the periphery the number of bisexual flowers decreases and does so much more rapidly than the number of male flowers. Hence the inner umbellules are often entirely male while the outer ones bear a number of bisexual flowers.

This rule is not without exception, however. There are namely Umbelliferae in the umbels of which the central umbellule occupies the top of the principal axis of the umbel and may consequently be distinguished as the top-umbellule.

Such top-umbellules are especially found with *Carum Carvi* and *Oenanthe fistulosa* and occasionally, although not so regularly, also with *Daucus Carota*. For such a top-umbellule now the rule does not hold that the part occupied by the male flowers is greater than in the surrounding umbellules. Such an umbellule contains a greater quantity of bisexual flowers. With *Carum Carvi* I often found no male flowers in the top-umbellule when all others, as well the peripheral as the more inwardly situated umbellules had some of them. In other specimens the number of male flowers in this top-umbellule was smaller than in the other.

Of *Oenanthe fistulosa* the umbels of the second order are in this country much larger than those of the first order; they consist of five to eight umbellules and agree in their constitution almost entirely with that, indicated by SCHULZ for the umbellules of the first order. Here as a rule a top-umbellule can be very easily distinguished; it contains only a few (7 to 9) male flowers, but is for the rest entirely

hermaphrodite, while the side-umbellules are generally exclusively male.

With *Daucus Carota*, where the umbellule as was remarked above, often consists of no more than one flower, this latter is very often hermaphrodite, also when the surrounding umbellules consist entirely of male flowers.

It must still be remarked for the andro-monoecious Umbelliferae that both sorts of flowers as a rule occupy a fixed place in the umbellule.

In by far the most Umbelliferae the bisexual flowers are found near the edge and the male ones in the middle.

Only a few make an exception to this rule; with *Oenanthe fistulosa* and *Sanicula europaea* the opposite is found and with *Astrantia* the bisexual flowers as a rule occupy a definite zone between the peripheral and central male flowers. Advancing from the circumference to the centre we find there first one or two whorls of male flowers, then a whorl of bisexual ones and finally at the centre male flowers again.

But although it may be the rule for all other Umbelliferae that in all the umbellules, containing the two forms of flowers, the hermaphrodite ones are placed at the edge and the male ones in the middle, an exception must be made for those Umbelliferae which in the middle of the umbellules develop a top-flower, for this latter is as a rule bisexual.

Such top-flowers are e.g. regularly found with *Chaerophyllum* and with *Meum*; in each umbellule of *Chaerophyllum temulum* and *Meum athamanticum* bisexual marginal flowers and a bisexual top-flower are found and for the rest male flowers.

Also with *Aegopodium Podagraria*, *Carum Carvi* and *Daucus Carota* bisexual top-flowers are found in the umbellules, but in these species this top-flower is not always found in all umbellules.

No extensive argument will be needed to understand that the two forms of flowers, found in the same individual of the plants mentioned, may be considered, like the two flowers of a cleistogamic plant, as two antagonistic characters which mutually exclude each other and that consequently these plants may be compared with ever-sporting varieties, originated by mutation, the existence of which was shown by DE VRIES.

Every andro-monoecious Umbellifera of which we compare a number of individuals among themselves, affords an opportunity for noticing that the two antagonistic characters evidently fight for

supremacy, in which combat now one, then the other gains an advantage.

But if of a species which is rich in forms we mutually compare a fairly complete series of andro-monoecious forms, we are struck by the circumstance that between these and the ever-sporting varieties known until now, there is this important difference that while with other ever-sporting varieties the original specific character is always more conspicuous than the racial character, here very often the opposite takes place.

We met in what precedes plants like *Myrrhis odorata*, *Meum athamanticum* or forms of *Pastinaca sativa*, *Heracleum Sphondylium* and *Daucus Carota*, where the specific character had been entirely superseded by the racial character, and this raises the question whether the andro-monoecious Umbelliferae, looked upon as races originated by mutation, must be placed on a line with the above-mentioned gyno-monoecious *Satureja hortensis* and other ever-sporting varieties.

We know from the theory of mutation that the interaction of two antagonistic characters may show itself in more than one way and that a character originated by mutation may be inherited in a different degree in various plant-species, by which process various races are formed.

To a race in which the anomaly comes only little to the front, much less than the normal character, and which consequently is hereditary in a small degree only, DE VRIES has given the name of a half-race, and the abnormal character he has called *semi-latent*. That, however, among these half-races important differences may occur in the measure in which the character is semi-latent, clearly appeared from the statistical investigation of the half-races, e.g. of *Trifolium incarnatum quadrifolium* and *Trifolium pratense quinquefolium*.

It may be imagined that there exist races in which the two antagonistic characters possess nearly the same degree of heredity so that then it is often difficult, under favourable circumstances, to settle whether the specific or the racial character is more prominent and sometimes even, when the conditions of life are very favourable, the anomaly gets the upper hand. In such a race as well the specific character as the anomaly are then to be considered as *semi-active*. The statistical investigation of the anomalies has not yet revealed that such races really exist.

But it may be further imagined that between these latter races which DE VRIES called middle-races and the constant varieties, in which the specific character is latent and the anomaly active, there

exist still other races in which the *normal character* is semi-latent to a different degree.

DE VRIES thinks such cases possible, but until now they have not yet been noticed ¹⁾. Now the question arose to me whether in the andro-monoecious Umbelliferae we may not have such races in which the specific character has become semi-latent? ²⁾

Let us start our speculations with one of those Umbelliferae of which besides andro-monoecious ones also hermaphrodite and male forms are known, e. g. *Heracleum Sphondylium*.

As was remarked above, *Heracleum Sphondylium* appears in a great part of Middle Europe as a hermaphrodite plant. In the environs of Neu-Ruppin at the same time forms are however found which are only bisexual in the umbels of the first order, whose umbels of the second order are composed on half bisexual and half male umbellules and whose umbels of the third order are exclusively male, and which in consequence may be considered to produce about as many male as bisexual flowers.

In this country now I found besides the hermaphrodite and the Neu-Ruppin middle forms a great variety of forms which may be considered either as gradual transitions of those middle forms to perfectly hermaphrodite ones or as gradual transitions of those middle forms to perfectly male individuals, which latter occur also in this country.

If we now *for the present* consider this andro-monoecious plant which is so rich in forms as an ever-sporting variety, and if we compare its properties with those of *Trifolium pratense quinquefolium*, which has first been extensively dealt with by DE VRIES, and later has been investigated in all its details by Miss TAMMES ³⁾, so that of this race the properties are most completely known, then we begin with asking what peculiarities *Heracleum* should present if its monoecious form represented an ever-sporting variety.

Then we should observe:

1. that a strongly developed specimen, e.g. a plant with umbels of the first to the fourth order, produces more male flowers than an individual which has not succeeded in getting beyond the formation of umbels of the first and second order.

¹⁾ DE VRIES, Mutationstheorie, I, p. 424.

²⁾ In my article on cleistogamic plants I already briefly raised the question whether *Ruellia tuberosa*, *Impatiens noli tangere*, *Impatiens fulva*, *Amphicarphaea monoica*, *Viola spec. div.* are not in this condition.

³⁾ Bot. Zeit. 1ste. Abt., Heft XI, 1904.

2. that plants on fertile soil produce on the whole more male flowers in proportion to the bisexual ones than plants on less fertile soil.

3. that the male flowers only appear at a stage in which the plant has grown stronger, that they gradually increase in number as the individual grows stronger and gradually decrease in number again when the plant has passed its highest point of development.

4. that in each umbel as well as in each umbellule which contains both forms of flowers, the male flowers are preferably found in those places which are most favourable with respect to nutrition.

It is not difficult to show that observation does *not* confirm these four points.

Let us in the first place consider point 4.

There can be no doubt that (excepting the just mentioned terminal umbellules and terminal flowers) the peripheral umbellules are more favourably placed with regard to nutrition than the more inwardly situated umbellules, and that in each umbellule the flowers at the circumference also occupy a more favourable position than those in the middle. This is seen not only by the inner umbellules being less rich in flowers but also in the flowers becoming smaller the further they are distant from the periphery; often the central flowers do not reach their normal development or the setting of the fruit does not take place. We see here the same with the umbels as with long-drawn inflorescences like those of *Capsella Bursa pastoris* or *Pisum sativum*, that namely the last-formed flowers, at the top of the inflorescence, no longer reach their normal development on account of insufficient nutrition. Further every umbellule (not only a mixed one but also a purely hermaphrodite one) allows us to notice that the peripheral flowers are ahead of the central ones in their development.

And now we see with all Umbelliferae without exception:

that the peripheral umbellules retain their bisexual character longest,

that the male flowers always occur first at the centre of the umbel,

that where the umbellules are mixed, the number of bisexual flowers always decreases from the periphery to the centre,

that the inner umbellules often are already entirely male when the outer ones still contain bisexual flowers, and

that everywhere, except with *Oenanthe fistulosa*, *Sanicula europaea* and *Astrantia* the marginal flowers in the umbellules are bisexual and the central flowers male¹⁾.

¹⁾ I think an explanation may be found for the anomalous behaviour of these three genera. I cannot dwell on this point, however, in this short communica-

In other words, we may say that as well in the umbel as in the umbellule the bisexual flowers always occupy the place which is most favourable with respect to nutrition.

That terminal umbellules and flowers are placed most favourably is evident; it can be readily explained why a top-umbellule is often richer in bisexual flowers than other umbellules from the centre and why as a rule the top-flower of the umbellule is hermaphrodite.

That this position is by far the most advantageous can also be inferred from the fact that often the top-flower is the only bisexual one of the whole umbellule. So with *Meum athamanticum* e.g. it is very often found that in the umbels of the second order, the 6—8 inner umbellules possess no bisexual flowers at all; the only bisexual flower of these umbellules is the top-flower.¹⁾

So we see exactly the opposite from what we should observe if the andro-monoecious plant represented an ever-sporting variety like *Trifolium pratense quinquefolium*. It is not the male flower — the anomaly — which is preferably found in the best places, but the bisexual flower, and on further examination of the above points 1, 2 and 3 we shall again see how it is this latter that depends on the nutritive conditions and in all respects behaves like a character in a semi-latent condition opposed to the active condition of the anomaly.

I pointed out already that with all andro-monoecious Umbelliferae the umbel of the first order shows the anomaly least.

With very many forms the male flower appears first in the umbels of the second order, with others in those of the third order, and sometimes it is the umbel of the fourth order in which the male flower appears first.

But where these flowers are already observed in the umbels of the first order their number is there always less than in the umbels of the second and higher orders.

The umbel of the first order consequently retains in all andro-monoecious Umbelliferae the pure racial character longest.

If we remember that the umbel of the first order is at the same time the terminal umbel of the plant and is extremely favourably placed at the end of the principal axis with regard nutrition, we cannot wonder at this, bearing in mind what was said when

tion. I shall return to it elsewhere when exposing the differences between the forms occurring in this country and those that have been observed in other parts of Europe.

¹⁾ This reminds us of what may be noticed with *Echinophora spinosa*. Vide supra.

discussing point 4. We find the already stated conception confirmed that *the bisexual flower, being in a latent condition with respect to the anomaly, preferably occurs in the most favourable places.*

We may also assume that the plant during the flowering of its top-umbel, which only occurs after it has reached its full vegetative development, is also in the strongest stage of its growth, in a stage in which a good part of its nutritive material may be spent on the development of its top-umbel, while all umbels that bud forth later, are in less favourable conditions, first on account of their being placed on lateral axes of the second or higher order and secondly because a very great part of the nutritive material is spent on the ripening of the fruit of the first umbel during the development of the umbels of the second or at any rate higher orders. This would explain why in the umbel of the second order the semi-latent bisexual flower is no longer prominent in the same degree as in the terminal umbel, and why in the umbels of the third and fourth order it more and more gives way before the racial character.

This also explains why in very strong specimens the male flowers first appear in the umbels of the third order, and why often with *Sium latifolium*, *Daucus Carota* and others, not until late in summer, when the plant has already passed its highest point of development, male flowers and even male umbels appear in plants which in their umbels of the first and second or first, second and third order have exclusively produced bisexual flowers.

That in fact strongly developed specimens produce more bisexual flowers than weak specimens was already noticed by MAC LEOD. With strong specimens — he says in his note on *Aegopodium Podagraria* — the umbels of the first order and with very strong specimens also those of the second order consist almost exclusively of hermaphrodite flowers, while with ordinary specimens the umbellules in the umbels of the first order consist partly and in those of the second order exclusively of male flowers. Also SCHULZ made the same remark with *Torilis Anthriscus* and *Pimpinella saxifraga* and personally I found the justness of his remark repeatedly confirmed with *Pimpinella magna*, *Aegopodium Podagraria*, *Aethusa Cynapium*, *Astrantia major* etc.

If now finally the numerical relations of the two flower-forms are examined in umbels of such species as are found in large numbers on soils of different constitution and fertility, the examination at once shows that the number of bisexual flowers in a fertile place is considerably greater than in a less fertile one. *Anthriscus silvestris* and *Chaerophyllum temulum* are plants which in our country are

very general as well on sandy soil (at the edge of the dunes) as on fertile claygrounds. Both plants can be best judged by the constitution of the umbels of the second order.

Of *Anthriscus silvestris* the average constitution is :

	on sandy soil	on clay ground
of the six outer umbellules	4-5♀+11-13♂	7-10♀+3-4♂
of the seven inner umbellules	2-4♀+ 8-11♂	6-7♀+4-7♂

And of *Chaerophyllum temulum* :

of the outer umbellules	15♀+10♂+1♀	20♀+7♂+1♀
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while the 2 or 3 innermost umbellules of the plants on sandy soil are entirely male.

So the results are in perfect agreement with my observations on the influence of the fertility of the soil on the appearance of chasmogamic flowers with *Ruellia tuberosa* at Batavia and with those of GOEBEL on the chasmogamic flowers with *Impatiens noli tangere* in places of different fertility near Ambach ¹⁾.

From what has been communicated here it appears that the andromonoecious Umbelliferae in the natural state have the character of ever-sporting varieties in which the racial character, the bisexual flower, is in a semi-latent condition.

By assuming this it becomes clear why the anomaly shows itself least in the terminal umbel, why, after it has once appeared, it increases in number in the umbels of higher order, why in each umbel the number of hermaphrodite flowers decreases from the periphery to the centre, why in each umbellule the bisexual flowers are placed at the circumference and the male ones at the centre and why with those species in which the umbels have a top-umbellule, this latter often has again relatively more bisexual flowers than the surrounding umbellules and finally why, where in the umbellules a top-flower is found, this is as a rule bisexual and holds out longest when the umbellules grow more and more male, so that it often still occurs in such umbellules where the bisexual marginal flowers have already had to give way to the male ones.

Although I am of opinion that many things plead for my conception, yet I am perfectly aware that *certainly* about the true nature of the race, about the influence of fluctuating variability on the numerical relations between bisexual and male flowers, about the question whether perhaps locally different varieties or ever-sporting varieties

¹⁾ GOEBEL. Die kleistogamen Blüten und die Anpassungstheorien. Biol. Centralbl. Bd. XXIV. No. 24, p. 770.

may exist of one and the same Umbellifer and other related questions can only be obtained by culture experiments and statistical investigation.

Yet I thought it worth while to communicate these observations although they must only be considered as an exposition of the grounds why culture experiments were undertaken. It may be useful to indicate these grounds, first because they support my conception about the racial character of many cleistogamic plants, and further because in my opinion we may certainly expect that besides monoecious and cleistogamic plants, other plants in the natural state will turn out to have the character of races originated by mutation, so that this communication may to some extent draw attention to this point.

The culture experiments will from the nature of the case occupy a few years.

In the *Ergänzungsband* of *Flora* 1905, Heft I, p. 214, GOEBEL communicates as a sequel to his paper "Die kleistogamen Blüten und die Anpassungstheorien" the results of his continued culture experiments with cleistogamic species of *Viola*. The results of his experiments confirm his formerly pronounced opinion that the appearance of a cleistogamic or chasmogamic flower depends entirely on *nutritive conditions*. If these are favourable the chasmogamic flower is seen to appear; in the opposite case the cleistogamic one appears.

I communicated in my former article my objections to this conception. I will now only remark that the influence of the nutritive conditions shows itself in such a way that with favourable conditions the *semi-latent* character is developed, and with unfavourable is suppressed.

Now if in GOEBEL's experiments the chasmogamic flowering is suppressed when the plant is under unfavourable conditions, this is because *Viola* is an ever-sporting variety in which the chasmogamic flower is in a semi-latent condition. If the cleistogamic *Viola* belonged to one of the other ever-sporting varieties, if e.g. it were an ever-sporting variety like the gyno-monoecious form of *Satureja hortensis* or *Trifolium pratense quinquefolium* in which the *anomaly*: (the female flower and the composite leaf) is in a semi-latent condition, then under favourable nutritive conditions the anomaly, the *cleistogamic* flower and under less favourable conditions the *chasmogamic* flower would be fostered.

Zoology. — "*The uterus of Erinaceus europaeus L. after parturition*". By Prof. H. STRAHL, of Giessen. (Communicated by Prof. A. A. W. HUBRECHT).

(Communicated in the meeting of March 31, 1906).

Through the obliging kindness of my colleague Prof. HUBRECHT, to whom I owe my sincere thanks, I was enabled to continue my researches on the involution of the uterus post partum with a species which, as far as I know, had not yet been studied in this respect. The examination of a larger number of uteri of *Erinaceus europaeus L.* made it possible sufficiently to investigate the regressive development in question.

In the pregnant uterus of the hedgehog shortly before parturition, pretty large foetal chambers are found, as was shown by HUBRECHT's extensive investigations. These chambers are entirely lined with epithelium which extends a little under the edges of the discoid placenta, the relative size of which is not very large. This placenta consequently belongs to the stalked ones, although the stalk is a very broad one.

The wall of the uterus of a hedgehog which was killed immediately after parturition is accordingly almost entirely covered with an epithelium which proved to consist of high, cylindrical cells. A layer of epithelium is only wanting in a small antimesometral region which is characterised as the site of the placenta by the large vascular stumps.

Excepting the specimen just mentioned the time post partum could not be determined in my preparations. So I had to arrange them in a series according to the thickness of the uteri, beginning with such as were still very thick and admitted of a determination of the number of former foetal chambers by swellings corresponding to the placental places and ending with others the appearance of which did not reveal any traces of pregnancy. The sections obtained from such uteri were in good agreement with each other and gave a sufficient idea of the various stages of involution.

I will not give here a detailed description of the phases of the retrograde development but only remark that the essential changes occur in the connective tissue of the uterine mucous membrane and in the glandular apparatus. The surface epithelium which with many animals (e.g. with *Putorius furo*) undergoes considerable changes of form, here shows these to a relatively smaller extent. They are limited to the casting off of superfluous parts and to the change of larger cells into smaller ones.

The epithelial defect of the placental spot is covered by epithelium advancing from the edges by a similar process as has become known of late years for a number of other mammals. Since a spot without epithelium is found in several stages, it must be assumed that the covering of the gap does not take place so rapidly as e.g. in many Rodents.

Characteristic for the connective tissue is the great abundance of liquid in it; after parturition it appears to be of a loose irregular texture and contains a considerable number of large blood- and especially lymph-vessels, the former especially in the placental spot, the latter spread over the whole mucous membrane. In this connective tissue during the first period following parturition only small and irregularly shaped glands are found, with a low epithelium. These glands occupy little place in the pretty thick mucous membrane.

In the completely retrograde uterus I find a mucous-connective tissue which is not particularly strong and is rich in cells; in this long glands reach in a very graceful and regular arrangement from the inside of the uterus to the musculature, while larger blood- and lymph-vessels are lacking in it. (see fig. 1 in HUBRECHT's *Studies in Mammalian Embryology*, Quart. Journ. of micr. sc. vol. XXX. new ser.). A comparison of these two stages, representing the beginning and the end of the involution, shows the direction of the involution. It consists, not to speak of the just mentioned minor changes in the epithelium, in the connective tissue becoming more compact, the total calibre becoming considerably less, and in a re-arrangement of the glandular apparatus which is probably accompanied by a new-formation, but certainly with a re-arrangement and considerable lengthening of the single glandular tubes.

In the connective tissue it is not so much the single cells which change (as is e.g. conspicuously the case with the female dog post partum) as there is a clear indication that intercellular substances diminish, which finally leads to a consolidation of the whole tissue.

At the same time the swollen lymph-vessels become smaller and narrower as well as the stumps of the torn blood-vessels in the placental spot, the trombi of which organise themselves. The retrogression at the placental spot takes place distinctly more slowly than in the remaining mucous membrane so that the placental spot is still recognised as something particular when the gap in the epithelium has become completely covered.

The return of the glands to their regular form takes still more time than that of the connective tissue, perhaps its last phase only sets in with a new rut.

Comparing the puerperal involution of the uterus of the hedgehog with the same process as it occurs in other mammals, hitherto studied, we may state that in this respect the hedgehog occupies an intermediate position between Rodents and Carnivora. It stands near the former in the way in which the epithelium regresses, near some of the latter in the regression of the layer of connective tissue, although in this respect the analogy is not complete.

The more accurate details of the involucional processes of which a short sketch is given here, will be published elsewhere.

Physics. — "*Magnetic resolution of spectral lines and magnetic force*". By Prof. P. ZEEMAN. (First part).

The intensity of a magnetic field may be defined by the amount of splitting up of a given spectral line emitted by a source placed in the field.

The distance of the outer components of a triplet can be measured with great accuracy. The components of a line resolved by the action of magnetism are of the same width as the original line and the high degree of accuracy obtainable in the measurement of spectrum photographs is generally known.

We may call two magnetic intensities equal, when producing equal amounts of separation of a spectral line, and we may call two differences of magnetic intensities equal, when the changes of the distances of the components are the same. In this way we obtain a scale of magnetic forces, the zero point and the magnitude of the units can still however be chosen arbitrarily. All conditions necessary for the *indirect* comparison of different intensities of a quantity are fulfilled.¹⁾

In this method of measuring magnetic forces we adopt a natural unit of magnetic force.

In applying the specified method we need not know the functional relation between magnetic force and magnetic separation of the spectral lines. It is sufficient to know that this function is one-valued. The most accurate measurements of the present time²⁾ and also theory render it extremely probable that the separation of the spectral lines is proportional to the intensity of the field wherein the source of light is placed. If this simple relation be

¹⁾ Comp. RUNGE, Maass und Messen. Encyclopädie der mathematischen Wissensch. Bd. V. I. 1903.

²⁾ See specially: A. FÄRBER, Über das Zeeman-Phänomen. Ann. d. Phys. 9 p. 886. 1902.

the true one, then our scale of magnetic forces is identical with the one commonly used.

We may then deduce from a given separation of a well-defined spectral line the strength of a field in absolute measure, the constant of reduction being once for all determined.

In the measurements of FÄRBER ¹⁾ relating to the lines 4678 Cd and 4680 Zn (produced by a spark between zinc-cadmium electrodes) the constant of reduction could be determined with a probable error of far less than $\frac{1}{100}$.

This method and all methods used till now for measuring magnetic fields, give the intensity in a point. Or rather the mean value in a small area (often rather extensive) or in a small space is considered to be the intensity in a point of that area or of that space.

The magnetic separation of the spectral lines enables us *to measure simultaneously the magnetic force in all points belonging to a straight line.*

In my experiments vacuum tubes charged with some mercury and excited by a coil were used. The tubes had capillaries of 8 cm. length, the interior diameters varying between $\frac{1}{4}$ and $\frac{1}{2}$ mm. The shape of the tubes was that given by PASCHEN ²⁾, also used by RUNGE and PASCHEN in their investigation concerning the radiation of mercury in the magnetic field.

A very moderate heating is required for the passage of the discharge, the light in the capillary is then fairly intense, it becomes very brilliant as soon as the tube is placed in the magnetic field.

It was noticed that for a given vapour density there exists a definite intensity of field for which the luminosity is a maximum. This is easily seen when putting on the current of a DU BOIS half ring electromagnet. Owing to the large inductance (relaxation time 50") the intensity of the field rises gradually. If the vapour density in the tube is not too high, there is clearly one moment of maximum luminosity.

If with a given field the density of the vapour is well chosen, then only a very moderate heating of the tube is sufficient for keeping it luminous.

When the tube is placed between the conical poles of a DU BOIS electromagnet and in a plane perpendicular to the line joining the poles, there is of course a different field intensity in every point of

¹⁾ FÄRBER. l. c.

²⁾ PASCHEN, Eine Geisslersche Röhre zum Studium des ZEEMAN-effectes. Physik. Zeitschr. p. 478. I. 1900.

the tube. Analysing the light of the different points of the tube with a spectroscope, we find of course a different magnetic separation for every point.

We can however spectroscopically analyse *simultaneously* the light of all points of the tube.

We have only to focus an image of the tube upon the slit of the spectroscope. This spectroscope must satisfy one condition. This condition is that to every point of the slit there corresponds one point of the spectral image. In the case of a prism spectroscope, of an echelon spectroscope, and of a plane grating spectroscope, this condition is clearly fulfilled, but the concave grating mounted in ROWLAND'S manner forms an exception. The use of the concave grating necessitates in our case the employment of the method proposed by RUNGE and PASCHEN ¹⁾.

My experiments were made in the above manner.

To illustrate this method I shall take the blue line of mercury (4359), which divides into a sextet.

The distribution of the magnetic force in a plane perpendicular to the axis of a du Bois electromagnet with a distance of 4 mm. between the poles is mapped out in a spindle-shaped magnetogram, of which a part is reproduced in Fig. 1. This figure is from a negative enlarged 9 times. We may extinguish by means of a Nicol the light of the inner components. At both sides two narrow lines remain. Fig. 2 is a *natural* size reproduction of a magnetogram taken under the specified conditions. The duplication of the outer components is lost in the reproduction. The extension of the field, mapped out by this magnetogram, may be better understood if I observe that 1 mm. in the focal plane of the spectroscope corresponds to 1.80 mm. in the plane between the poles or 1 mm. in the latter plane to 0,556 mm. of the negative. Hence in Fig. 1 5 mm. corresponds to 1 mm. between the poles. The complete magnetogram gives the magnetic force in a line, 30 mm. in length. Using a lens of shorter focus we can represent, of course, a greater part of the field. In the middle of the field the magnetic force is about 24,000 C. G. S. A *comparison* of field strengths can be made with a decidedly higher degree of accuracy than that which is given above for an absolute measurement.

The method set forth above will be applied, of course, only in difficult cases. As long as our spectroscopes of great resolving power are rather cumbersome, no practical application of the method is possible.

In many cases there will be great advantage in selecting a spectral line which is tripled in the field.

¹⁾ KATSER. Handbuch Bd. I, p. 482.

P. ZEEMAN. "Magnetic resolution of spectral lines and magnetic force."

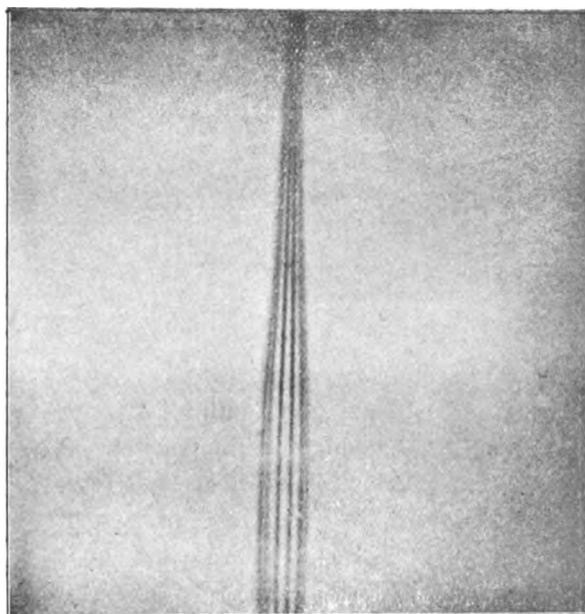


Fig. 1.

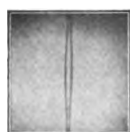


Fig. 2.

Proceedings Royal Acad. Amsterdam. Vol. VIII.

The magnetisation of the spectral lines enables us to determine the maximum value of the force with phenomena varying rapidly with the time, and with non-uniform fields.

In some cases it is of great importance to follow the behaviour of a spectral phenomenon with different strengths of field. The above described method might then be called *the method of the non-uniform field*.

In a future communication I hope to study in this manner the *asymmetry* of the separation of spectral lines in weak magnetic fields, predicted from theory by VOIGT. On a former occasion I have communicated some experiments giving rather convincing evidence of the existence of this asymmetry ¹⁾.

In the mean time, I think that the developments lately given by LORENTZ ²⁾ make it desirable to corroborate the reasons for accepting the existence of this extremely small asymmetry.

Mathematics. — “*Some properties of pencils of algebraic curves*”.

By Prof. JAN DE VRIES.

§ 1. Let A be one of the n^2 basepoints of a pencil (c^n) of curves c^n of order n , B one of the remaining basepoints. If we make to correspond to each c^n the right line c^1 touching c^n in A , then we get as product of the projective pencils (c^n) and (c^1), a curve T_1 of order $(n+1)$ forming the locus of the tangential points of A , i. e. of the points which are determined by each c^n on its tangent c^1 . This *tangential curve* has in A a threefold point where it is touched by the inflectional tangents of three c^n having in A an inflection; it has been considered for the first time by EMIL WEYR (Sitz. Ber. Akad. in Wien, LXI, 82).

I shall now consider more in general the locus T_m of the m^{th} tangential points of A . The order of this curve is to be represented by $\tau(m)$, whilst $\alpha(m)$ and $\beta(m)$ are to indicate the number of branches which T_m has in A and B .

Prof. P. H. SCHOUTE has drawn my attention to a paper inserted by him in the Comptes Rendus de l'Académie des sciences, tome CI, 736, where the corresponding curve is treated for a cubic pencil. I found that the numbers obtained there for $n=3$ appear from the results to be deduced here.

¹⁾ ZEEMAN. These Proceedings, December 1899.

²⁾ LORENTZ. These Proceedings, December 1905.

To determine the functions $\tau(m)$, $\alpha(m)$ and $\beta(m)$ I shall make use of an auxiliary curve already used by WERR, which might be called the *antitangential curve* of A . It contains the groups of $n(n-1)-2$ points A_{-1} , having A as tangential point; so it passes three times through A and once through all points B . So it has $(2n^2-n)$ points in common with any c^n , from which it is evident that it is of order $(2n-1)$.

§ 2. The $(m-1)^{\text{th}}$ tangential curve (A^{m-1}) of A is cut by the antitangential curve (A^{-1}) of A , save in the base points, in the points A^{m-1} having A as tangential point. Their number amounts to three less than the number of tangents which T_m has in A , so $\alpha(m)-3$; for, on the three c^n which have in A an inflection A coincides with one of its m^{th} tangential points.

The three inflectional tangents being also tangents of the curve (A^{-1}) , the tangential curve (A^{m-1}) and the antitangential curve (A^{-1}) have $3\alpha(m-1)+3$ points in common in A . In each base-point B lie $\beta(m-1)$ points of intersection. So

$$(2n-1)\tau(m-1) = \alpha(m) + 3\alpha(m-1) + (n^2-1)\beta(m-1). \quad (1)$$

A second relation is found by noticing that (A^{m-1}) has with the antitangential curve of B , save the basis, the $\beta(m)$ points in common for which B is an m^{th} tangential point. In B lie $3\beta(m-1)$ points of intersection, $\alpha(m-1)$ points of intersection lie in A , $\beta(m-1)$ in each of the other basepoints. So

$$(2n-1)\tau(m-1) = \beta(m) + \alpha(m-1) + (n^2+1)\beta(m-1). \quad (2)$$

With any c^n the locus T_m has, save the basis, only the $(n-2)^m$ points $A^{(m)}$ in common; so

$$n\tau(m) = \alpha(m) + (n^2-1)\beta(m) + (n-2)^m. \quad (3)$$

§ 3. To find a homogeneous equation of finite differences for the determination of $\tau(m)$ I eliminate from the three obtained relations the quantities $\alpha(m)$ and $\beta(m)$, and I find

$$n\tau(m) = n^2(2n-1)\tau(m-1) - (n^2+2)\{\alpha(m-1) + (n^2-1)\beta(m-1)\} + (n-2)^m.$$

Here the expression within braces can be replaced on account of (3) by $n\tau(m-1) - (n-2)^{m-1}$. Then

$$\tau(m) = (n^2-n-2)\tau(m-1) + (n+1)(n-2)^{m-1}. \quad (4)$$

So

$$\tau(m-1) = (n^2-n-2)\tau(m-2) + (n+1)(n-2)^{m-2}. \quad (5)$$

Equations (4) and (5) finally furnish

$$\tau(m) - (n-2)(n+2)\tau(m-1) + (n-2)^2(n+1)\tau(m-2) = 0 \quad (6)$$

To determine a particular solution $\tau(m) = x^m$ we have

$$x^2 - (n-2)(n+2)x + (n-2)^2(n+1) = 0,$$

therefore

$$x = n^2 - n - 2 \text{ or } x = n - 2.$$

Consequently the general solution is

$$\tau(m) = c_1(n^2 - n - 2)^m + c_2(n - 2)^m.$$

To determine the constants c_1 and c_2 I substitute in (4) the known values $(n+1)$ of $\tau(1)$ and $(n+1)(n^2-4)$ of $\tau(2)$.

Now

$$\begin{aligned} n+1 &= c_1(n^2 - n - 2) + c_2(n - 2), \\ (n^2 - 4)(n+1) &= c_1(n^2 - n - 2)^2 + c_2(n - 2)^2. \end{aligned}$$

Finally we find by elimination of c_1 and c_2

$$\tau(m) = (n+1)(n-2)^{m-1} \frac{(n+1)^m - 1}{n} \quad . \quad . \quad . \quad (7)$$

From (1) and (2) ensues

$$\alpha(m) - \beta(m) = -2\{\alpha(m-1) - \beta(m-1)\},$$

so

$$\alpha(m) - \beta(m) = (-2)^{m-1}\{\alpha(1) - \beta(1)\} = -(-2)^m \quad . \quad . \quad (8)$$

Making use of (3) and (7) we now find

$$n^2 \alpha(m) = (n-2)^{m-1}\{(n+1)^{m+1} - 2n+1\} - (n^2-1)(-2)^m \quad . \quad (9)$$

$$n^2 \beta(m) = (n-2)^{m-1}\{(n+1)^{m+1} - 2n+1\} + (-2)^m \quad . \quad . \quad . \quad (10)$$

§ 4. For $m=2$ we find $\alpha(2) = n^2 + n - 9$; as A is inflection for three curves c_n , there are therefore $(n^2 + n - 12)$ curves on which A coincides with its second tangential point. From this ensues the wellknown result that A is point of contact of $(n+4)(n-3)$ double tangents.

In a former paper ¹⁾ I have brought into connection the locus of the points of contact D of the double tangents with the locus of the points W in which a c^n is cut by its double tangents. To determine, how often a point D coincides with one of its tangential points W I consider the correspondence of the rays $d = OD$ and $w = OW$ which the correspondence (D, W) forms in a pencil with vertex O .

As the curves (D) and (W) are of orders $(n-3)(2n^2+5n-6)$ and $\frac{1}{2}(n-4)(n-3)(5n^2+5n-6)$, to each ray d correspond $(n-4)(n-3)(2n^2+5n-6)$ rays w and to each ray w correspond $(n-4)(n-3)(5n^2+5n-6)$ rays d .

¹⁾ "On linear systems of algebraic plane curves." Proc. April 22 1905, Vol. VII (a), p. 711.

Because each of the $2n(n-2)(n-3)$ double tangents out of O represents $2(n-4)$ coincidences $d \equiv w$, the number of coincidences $D \equiv W$ is represented by

$$(n-4)(n-3)(2n^2+5n-6) + (n-4)(n-3)(5n^2+5n-6) - 4(n-4)(n-3)(n-2)n = 3(n-4)(n-3)(n^2+6n-4).$$

In a pencil (c^n) we find that $3(n-4)(n-3)(n^2+6n-4)$ curves have an inflection, of which the tangent touches the curve in one other point more.

In the paper quoted above I thought I was able to determine this number out of the points of intersection of the curves (D) and (W); here I overlooked the fact that a point of contact of a double tangent can be tangential point W of another double tangent.

§ 5. To find the number of threefold tangents I consider the correspondence between the rays projecting out of O two points W and W' lying on the same double tangent. The characterizing number of this symmetric correspondence is evidently equal to $\frac{1}{2}(n-4)(n-3)(5n^2+5n-6)(n-5)$, whilst each double tangent borne by O replaces $2n(n-2)(n-3)(n-4)(n-5)$ coincidences. The number of coincidences $W \equiv W'$ amounts thus to

$$(n-5)(n-4)(n-3)(5n^2+5n-6-2n^2+4n).$$

As each threefold tangent bears three of these coincidences we have the property:

In a pencil (c^n) we find that $(n-5)(n-4)(n-3)(n^2+3n-2)$ curves have a threefold tangent.

§ 6. In my paper indicated above I have tried to determine the number of undulation-points out of the points of intersection of the inflectional curve (I) with the locus of the points (V) which c^n determines on its inflectional tangents. As each inflection which is also tangential point of another inflection is common to (I) and (V), the number found elsewhere is too large. The exact number I can determine by means of the correspondence between the rays OI and OV .

As the orders of (I) and (V) are $6(n-1)$ and $3(n-3)(n^2+2n-2)$ and each of the $3n(n-2)$ inflectional tangents drawn from O replaces $(n-3)$ rays of coincidence, we get for the number of coincidences $I \equiv V$

$$6(n-1)(n-3) + 3(n-3)(n^2+2n-2) - 3n(n-2)(n-3) = 6(n-3)(3n-2).$$

In a pencil (c^n) we find that $6(n-3)(3n-2)$ curves have a four-point tangent.

§ 7. The curve of inflections (I) and the bitangential curve (D) have in each of the $3(n-1)^2$ nodes of (c^n) in common a number of $2(n-3)(n+2)$ points.

For, out of a node we can draw to the c^n to which it belongs $(n^2 - n - 6)$ tangents, to be regarded as double tangents, whilst each node of a c^n is at the same time node of (I).

In each basepoint lie moreover $3(n+4)(n-3)$ points of intersection (§ 4). The remaining points common to (D) and (I) are the inflections of which the tangent touches the c^n once more (§ 4) and the undulation-points (§ 6) where the two curves touch each other.

Indeed, we have

$$\begin{aligned} &6(n-1)^2(n-3)(n+2) + 3n^2(n+4)(n-3) + 3(n-4)(n-3)(n^2+6n-4) + \\ &+ 12(n-3)(3n-2) = 6(n-1)^2(n-3)(n+2) + 3(n-3)(2n^2+6n^2-16n+8) = \\ &= 6(n-1)(n-3)(2n^2+5n-6), \end{aligned}$$

and this is the product of the orders of (I) and (D).

Physiology. "*On the strength of reflex stimuli as weak as possible.*"

By Prof. H. ZWAARDEMAKER. (Report of a research made by D. I. A. VAN REEKUM).

(Communicated in the meeting of March 31, 1906).

Investigated were chemical, thermal, mechanical and electrical stimuli, which partly acted upon the skin partly on the sensible nerves of the animals, which were experimented on.

§ 1. The chemical stimuli were applied by immersing the hind-leg of a winterfrog in a little bowl with a solution of sulphuric acid varying from $\frac{1}{4}$ to $\frac{1}{100}$ % $\left(\frac{n}{20} \text{ to } \frac{n}{160}\right)$. The spinal cord system was withdrawn in the usual way from the influence of the cerebrum. After the experiment the legs were washed with distilled water and the experiment repeated after a pause of 5 minutes. Neglecting the preliminary reflex, only a complete reflex was considered as a positive result. After-reflexes and general movements did only show themselves when rather strong concentrations were used.

As a rule a $\frac{1}{100}$ % $\left(\frac{n}{85}\right)$ solution of sulphuric acid may be accepted as the minimum stimulus which still produces reflexes. The reflex-

time at an immersing of the two legs was 10 seconds, at an immersing of one leg 22 seconds.

It was calculated how much sulphuric acid disappeared in the skin of the frog, when $\frac{1}{11}$ % sulphuric acid $\left(\frac{n}{85}\right)$ was used, respectively how much was fixed by the excretion-products. This occurred by titrating the immersing liquid with caustic soda (methylene orange as indicator) before and after a series of 20 singular reflexes.

Then it appears that about $\frac{1}{11}$ of the total quantity of the used sulphuric acid has been bound. Supposing the heat of reaction of 2 aequivalents natron and 1 aequivalent sulphuric acid to be 31,4 great calories and supposing that our sulphuric acid has been bound in a reaction of this kind then the heat of reaction of the chemical process pro singular reflex, reckoned over the whole immersed surface of the skin, amounts to 1,37 gram-calorie. It is evident that only a small part of this supposed reaction can have taken place in or near the terminations of the nerves and that this value of 1,37 gram-calorie must be also a limit under which is situated the heat of reaction.

This amount may surpass the real value of the reflex-stimulus perhaps a million of times. By measuring the electrical conductivity of the stimulating solution before and after the reflexes it was controlled if anything else had passed into the immersing liquid in the place of the disappeared sulphuric acid. This proved to be the case for the increase of resistance of the liquid experimented with, was greater than would follow from the decrease of the sulphuric acid.

§ 2. As a thermal stimulus served immersion in cold or warm water. The most favourable result was obtained by a decreasing difference of temperature between animal and water of 10° C. and by an increasing difference of temperature of 15° C. The reservoir, isolated by an asbestos envelope, in which the immersion of the frog took place contained 50 ccm. The immersion was performed once and after that the reflex was waited for. Then it could be stated that the temperature of the water increased on an average of 8 centigrades by the immersion of the heated frog and decreased on an average of 22 centigrades by the immersion of the leg of a frog which was cooled down. Some experiments already gave a reflex before it had come to this. A sufficient quantity of reflexes large enough to avoid casualties, were accompanied by an increase of temperature of 7 centigrades resp. a decrease of temperature of 19

centigrades. Consequently at these last experiments a quantity of heat of 3,5 gr. calorie must have been withdrawn from the leg of the frog, and 9,5 calorie have been added. This heat divided itself during a reflex-time of average $7\frac{1}{2}$ sec. resp. 9 sec. over the whole immersed part of the skin. Only a very small part will have come to the benefit of the terminations of the nerves and what appears as a reflex-stimulus may very well be millions of times smaller than the total quantity of the heat which is given or taken up. The above mentioned values have again only the significance of limit values beneath which the heat resp. cold stimulus, which causes a reflex movement, must be necessarily situated.

§ 3. To produce mechanical reflex-stimuli first falling mercury drops were made use of¹⁾, afterwards a little ball of resin fastened to a pig's-bristle, which by an electrically moved tuning fork of 16 double vibrations was kept in a forced vibration of fixed amplitude. In both cases as much as possible the lateral side of the foot, where the *corpuscula tactus* are situated, was taken.

The mercury drops were all of the same size (average 100 mgr.) and were used to the number of 1 to 15, trickling down one after the other. The height from which the drops were falling varied from 1 to 20 cm. At each experiment the *vis viva* was calculated with which the drop came down on the skin of the animal. It was obvious that for causing a reflex the *vis viva* had to be in minimo 686 ergs which amount was obtained by dropping 7 drops one after the other from a falling height of 1 cm. Once it was possible to obtain a reflex by the fall of one drop from a height of 7 cm. which shows the same quantity of energy now contained in one single stimulus without any summation.

The smallest results according to *vis viva* which still produce a reflex were obtained with a little ball of resin of 7 milligram which vibrated with an excursion of 5 mm. After a reflex-time of on an average 3 sec. the reflex movement was obtained. The quantity of energy which was added to the skin in this way in summing contains 212 ergs.

The result of the mechanical stimulation is quantitatively considerably lower than the above mentioned chemical and caloric stimulation. It leads to a minimum, which however put together in a restrict spot still possesses the peculiarity of having been communicated to a part of the skin which probably is considerably

¹⁾ E. A. SCHÄFER, Proc. Physiol. Soc. 26 Jan. '901.

larger than the surface of a corpusculum tactus. The divergency between the quantity of energy applied and that which is used for reflex-stimulus is in this last case not by far so great as in the thermal forms of reflex stimulus. The simplest relation might be expected in the very favourable case already mentioned, in which only one drop of mercury falling from a height of 7 cm. was used. Meanwhile, with the ball of resin, still smaller values were obtained, notwithstanding the summation was taken into the account, so that we may accept, this most simple case has not at all been a most favourable one.

§ 4. The electrical stimulation brought about by discharges of a condensator which was immediately before charged with a voltage varying between 0 and 2 volts. The capacity of the condensators, which were constructed in the laboratory from mica of different thickness and coverings of tinfoil different in surface varied from 15×10^{-5} to 4×10^{-3} m. F. They were wholly closed in by paraffine and verified by comparing with an air-condensator. The following stimuli were used: firstly on the skin of the leg of the frog by means of little catches of steel which surround the leg: secondly on the posterior roots of the lumbal-cord, by means of platinum-electrodes set in paraffine, thirdly on the nervus vagus of a rabbit by means of platinum-electrodes set in ebonite. The stimuli were for the greater part supplied in series with an interval of $\frac{1}{2}$ sec. in a number varying between 1 and 15. All those regulations took place automatically by properly isolated swings and keys. The best results gave a condensator of 59×10^{-5} m. F.

Skinreflexes (not ordered series)

(with condensator of $59 \cdot 10^{-5}$ m.F.)

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	number of stimuli
121	103	158	98	76	34	31	40	9	20	6	6	2	5	10	number of observat.
0.87	0.81	0.83	0.77	0.77	0.75	0.74	0.79	0.94	0.86	0.85	0.75	0.65	0.62	0.67	average voltage
22.33	19.35	20.32	17.49	17.49	16.59	16.15	18.41	26.07	21.81	21.31	16.59	12.46	11.34	13.24	energy in 10^{-4}

The above mentioned experiments were taken without a system. Observing a more judicious succession of the stimuli more favourable conditions of stimulation were obtained in the following series.

From this table it distinctly appears that the stimulus is limited to the smallest quantity of energy when a condensator $0,00035$ m. F. is used. Then $1,4 \times 10^{-4}$ ergs is sufficient on condition that the stimulus is repeated three times with an interval of $\frac{1}{2}$ sec. Consulting the experiments about reflexes which are not mentioned

Skinreflexes (ordered series)

(the average for the different condensators).

Capacity in m.F.	Voltage	Number of stimuli	Energy of each stimulus in 10^{-4} ergs.
0.00025	0.40	2	2.0
0.00035	0.28	3	<u>1.4</u>
0.00059	0.24	8	1.7
0.0013	0.24	3	3.7
0.004	0.34	15	23.1

in the tables a minimum value is obtained which is only slightly larger, namely an amount of 5×10^{-4} ergs.

The result got at the last root of the lumbal region with frogs cannot be given in one table as the individual experiments differed too much and have not been numerous enough to fix the average. In a very sensitive preparation when the above mentioned condensator of 0.00035 m. F. was used, a distinct reflex was obtained with a single discharge of only $8,6 \times 10^{-6}$ ergs, a result which shows clearly that in the experiments of Mr. VAN REEKUM the reflex sensitiveness has been considerably greater from the root than that from the skin. In a single case there was even found a value still three times smaller. The above stated number however was not obtained accidentally but represents a whole series of observations (12 in number).

By central stimulation of the cervical part of the nervus vagus of a rabbit reflex-changes of the breathing were caused, which could be registered by means of the aerodromograph¹⁾. The said reflex consists according to the intensity of the stimulus 1. if stimulating with very weak discharges in a slight increase of frequency of breathing and in an increase of the rapidity of the current of air in in- and expiration 2. if stimulating with somewhat greater discharges, an increase of the rapidity of the stream of air notwithstanding decrease of frequency 3. stimulating with sufficient great discharges a distinct decrease in rapidity of the stream of air and frequency both. If we only examine the result mentioned in the third case as the reflex on which we want to base our measurements, the results of the experiments may be taken together as follows:

¹⁾ H. ZWAARDEMAKER und C. D. OUWEHAND. Arch. f. Physiol. 1901. p. 241.

Breath-reflexes.

capacity in m.F.	15 successive discharges		1 discharge	
	voltage	energy of the stimulus in 10^{-4} ergs	voltage	energy in 10^{-4} ergs
0.00015	0.17	0.24	0.23	0.40
0.00025	0.13	0.21	0.21	0.55
0.00035	0.10	0.17	0.17	0.51
0.0059	0.09	0.24	0.16	0.76
0.0013	0.11	0.79	0.19	2.35
0.004	0.12	2.88	0.18	6.48

CONCLUSION.

The reflex stimuli of different kinds used as weak as possible on cold- resp. warmblooded animals have in minimo very different value. Thus one and the same effect was brought about by applying on the skin of a frog of an electric stimulus of $3,15 \times 10^{-4}$ ergs by a mechanical stimulus of 212 ergs, by a thermal stimulus of 11,5 mega-ergs and by a chemical stimulus of 57 mega-ergs. So of all these forms of stimulus the electrical is the most favourable. It may be still more favourable when we let the stimulus act not on the skin but on a posterior lumbal root of the frog. Then 3×10^{-6} ergs is sufficient to cause a typical reflex and so the amount approaches to that which occurs with weak sensorial stimuli (light stimuli vary in general between 1×10^{-10} as lowest and 6×10^6 as highest value; acoustical stimuli between $0,3 \times 3^{-8}$ as lowest and 1×10^9 as highest value¹⁾). What holds true for frogs, as a rule holds true for mammals. From the nervus vagus there can be brought about by central stimulation with an electrical stimulus of $0,17 \times 10^{-4}$ ergs a very marked change of breathing, whereas a few times smaller value causes an indistinct but yet an unmistakable acceleration of breathing. Here also the minimum reflex stimuli have a limit value of the order 1×10^{-6} ergs.

¹⁾ Die physiol. wahrnehmbaren Energiewanderungen, Ergebnisse der Physiologie Bd. IV. 1906. p. 423.

(May 25, 1906).

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